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Artykuły publikowane w tym zeszycie były przedstawione w czasie VI Międzynarodowej Konferencji Naukowej pt.: TOKSYCZNE SUBSTANCJE W ŚRODOWISKU, Kraków, 6–8 września 2010 r.

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Prezentowane artykuły przeszły normalną procedurę recenzyjną i redakcyjną.

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ECOLOGICAL CHEMISTRY AND ENGINEERING A

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Monika ARASIMOWICZ[1],
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POST-EFFECT OF BOTTOM SEDIMENT ADDITION TO THE SUBSTRATUM ON CHEMICAL COMPOSITION OF WHITE MUSTARD (*Sinapis alba* L.) BIOMASS

PART 1. MACROELEMENTS CONTENT

NASTĘPCZY WPŁYW DODATKU OSADU DENNEGO DO PODŁOŻA NA SKŁAD CHEMICZNY BIOMASY GORCZYCY BIAŁEJ (*Sinapis alba* L.)

CZ. 1. ZAWARTOŚĆ MAKROELEMENTÓW

Abstract: The paper aimed to investigate the effect of bottom sediment supplement to the substratum on chemical composition of cultivated plant biomass considering the optimal macroelements content in plants destined for fodder, as well as an assessment of potential bottom sediment utilization in agriculture. The researched material was the aboveground biomass of white mustard (*Sinapis alba* L.), cultivated in the third year after the application of bottom sediment dredged from the Roznow Reservoir to very light and very acid soil. The experiment was a continuation of research conducted in 2005 and 2006 on: Italian ryegrass (*Lolium multiflorum* L.) and maize (*Zea mays* L.), respectively. The proportion of sediment in the substratum was between 1 and 20 %.

Macroelements content in mustard shoot biomass was diversified depending on the share of bottom sediment in the substratum and ranged as follows: 36.8–47.1 g N, 2.25–5.20 g P, 7.52–47.47 g K, 26.25–42.50 g Ca, 2.3–4.5 g Mg and 1.11–4.67 g Na per 1 kg of dry mass. Among the analyzed elements the most diversified were content of K (V = 51.85 %) and Na (V = 44.53 %), less diverse were P (V = 23.27 %) and Mg (V = 19.73 %), whereas the least diversity was registered in case of N (V = 6.63 %) and Ca (V = 13.27 %).The highest contents of P, Ca and Mg were observed when the share of the sediment in the substratum amounted to 4 %, whereas mustard biomass accumulated the greatest quantities of N and Na when the sediment share in the substratum was 1 % and 3 %, respectively, while K contents were the highest on the control. Bottom sediment supplements to the substratum caused a decline in N, P and K contents at simultaneous increase in Ca and Mg content in mustard biomass in comparison with plants from the control object. A 7 % sediment supplement of the substratum caused an increase in Na content in mustard biomass, whereas a bigger admixture caused a decrease in this element content in comparison with the control.

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Obtained mustard shoot biomass on a majority of treatments revealed excessive contents of P, Ca and Mg and either excessive or too low contents of K and Na.

Applied bottom sediment led to the soil deacidification, positively affected plant yielding, so it may be used for improvement of light acid soils properties but the simultaneous control of plant chemical composition is necessary.

Keywords: bottom sediment, macroelements, N, P, K, Ca, Mg, Na, content

Bottom sediments are counted to by-products formed during recultivation of water reservoirs. Their granulometric composition contains considerable amounts of silt and clay fraction and also phosphorus, nitrogen and calcium compounds [1]. Waste materials such as bottom sediments, sewage sludge or furnace ashes may be a valuable source of minerals for crops. However, their concentrations of toxic substances should be taken into consideration because of their possible entering human food chain [2, 3]. The condition on which these materials may be used in agriculture is analyzing their chemical composition and testing their effect on yielding and quality of plant biomass [4].

Sediments develop on the bottom of a reservoir in result of accumulation of allochtonic deposits carried by the water feeding the reservoir and autochtonic deposits forming in the reservoir. Organic and mineral substances accumulate in bottom sediments. Intensive chemical and microbiological processes occur in their surface layer [5]. Chemical composition of the sediment depends on geological structure of respective catchment, morphological features of the reservoir, climatic conditions and the way of the area management [2].

The aim of the investigations was an assessment of usability of bottom sediment as a source of nutrients for plants and post-effect of its additions to the substratum on the essential macroelements content in the biomass of crops.

Material and methods

The experimental material was the aboveground biomass of mustard (*Sinapis alba* L.) cultivated in pot experiment in the third year after the application of bottom sediment dredged from the Roznow Reservoir to very light and very acid soil with granulometric composition of loose sand. Prior to the experiment outset, the sediment and the soil were dried in the open air, crushed mechanically and sifted. Subsequently their essential properties were assessed and the content of bioavailable P and K forms (Table 1).

Table 1

The basic properties of components of the substrate

Component	pH		Hh [mmol$^{(+)} \cdot$ kg^{-1}]	Organic C	Total N	Bioavailable	
						P_2O_5	K_2O
	KCl	H_2O		[g · kg^{-1}]		[mg · kg^{-1}]	
Sediment	7.20	8.31	—	3.65	1.19	41.3	116
Soil	4.40	5.86	12.2	4.73	0.524	94.3	246

The total content of macroelements was determined in soil and sediment (Table 2).

Tabela 2

Total content of macroelements in components of the substratum

Component	P	Mg	Ca	Na	K
	$[g \cdot kg^{-1}]$				
Sediment	0.532	3.833	17.46	0.973	8.632
Soil	0.333	0.565	1.002	0.091	0.915

Basic parameters of the soil and bottom sediment were determined using commonly applied analytic methods. The experiment was a continuation of former research conducted in 2005 and 2006, when the test plants were Italian ryegrass (*Lolium multiflorum* L.) and maize (*Zea mays* L.), respectively.

The bottom sediment, in doses constituting between 1 and 20 % of the substratum, was added to the soil, whereas the control treatment was very acid light soil without the sediment admixture (Table 3).

Table 3

Share of the components of the substratum in individual objects

Component	Share [%]												
Soil	100	99	98	97	96	95	94	93	92	91	90	85	80
Sediment	0	1	2	3	4	5	6	7	8	9	10	15	20

Substratum mass in each pot was 4 kg. Soil moisture during the experimental period was initially maintained on the level of 40 % and increased to 50 % and 60 % of MWC (*maximum water capacity*) with plant development. Plant vegetation period lasted from 24 April to 12 June. After the vegetation period the plants were harvested, dried and their macroelements contents were assessed using AAS and ICP-AES methods following dry mineralization and ash dissolving in HNO_3 (3:1, v/v).

Results and discussion

The yield of mustard aboveground biomass cultivated on the control treatment (soil without the sediment) was 1.01 g d.m. per pot (Fig. 1).

Admixture of bottom sediment to the soil caused increase in produced mustard aboveground biomass in comparison with the control treatment. The exception was the supplement constituting 1 % of the substratum mass, which caused an apparent worsening of yielding. On the other hand the admixtures of 2–20 % of the substratum mass led to almost linear increase in yields. Supplements of between 9 and 20 % caused significant increase in yields in comparison with the control treatment ($LSD_{0.05}$ = 0.74 g per pot). The yield of mustard shoots reached the highest mass of 8.6 g per pot when the

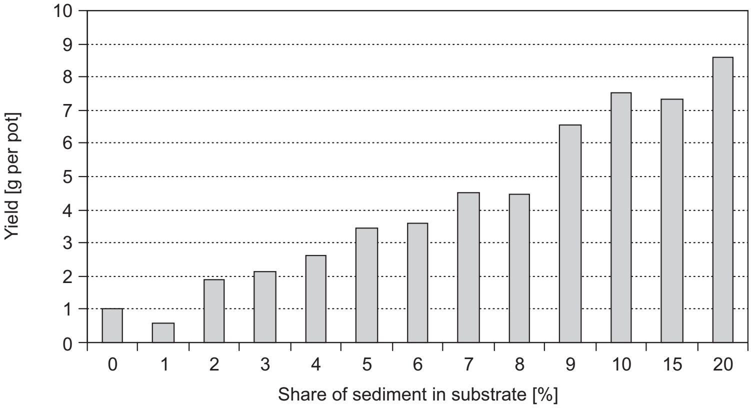

Fig. 1. Yield of the aboveground parts of mustard biomass depended on share of the bottom sediment in the substratum

share of bottom sediment in the substratum was 20 %. Average yield of the mustard shoots was 4.77 g per pot.

The content of N, P, K, Ca, Mg and Na in mustard shoots was presented depending on the bottom sediment share in the substratum. Macroelements content in plant biomass from individual treatments was distinctly diversified (Table 4).

Tabela 4

The statistic parameters of macroelements content in aboveground part of mustard

Parameter	N	P	K	Ca	Mg	Na
	Content [g · kg^{-1} d.m.]					
Minimum	36.8	2.25	7.52	26.25	2.3	1.11
Maximum	47.1	5.20	47.47	42.50	4.5	4.67
Arithmetic mean	42.08	4.16	22.07	34.08	3.58	2.50
Standard deviation	2.79	0.94	12.78	5.07	0.77	1.19
Coefficient of variation [%]	6.63	22.71	57.94	14.87	21.52	47.89

The most frequently stated limit values of macrolements content in plant material destined for animal feeds are: 3.0 g P, 17.0 g K, 7.0 g Ca, 2.0 g Mg and 1.5 g Na · kg^{-1} dry mass [6].

Nitrogen content in mustard shoot mass ranged from 36.8 to 47.1 g N · kg^{-1} d.m., on average 42.08 g N · kg^{-1} d.m. (Table 4, Fig. 2).

Average nitrogen content in plant biomass in the presented experiment was 1.5-fold higher than assessed by Traba et al [7] in legumes from permanent meadows in the San River valley and on the Dynowskie Uppland, on soils formed from alluvial deposits of a mountain river. The aboveground biomass of plant cultivated on the control treatment contained 45.7 g N · kg^{-1} d.m. and it was one of the highest contents in the analyzed plant material, whereas biomass of plants grown in the substratum with 1 % of sediment had the greatest amount of nitrogen (47.1 g N · kg^{-1} d.m.). Larger admixtures led to

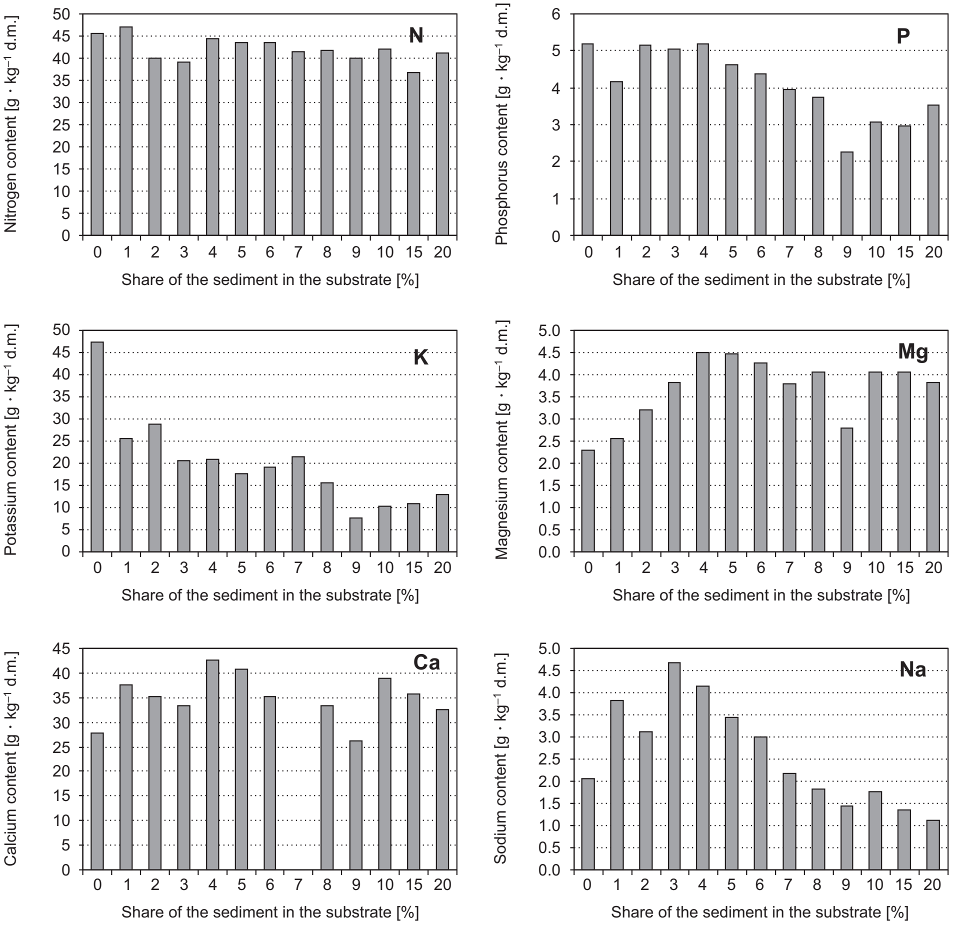

Fig. 2. N, P, K, Mg, Ca and Na content [g · kg^{-1} d.m.] in aboveground biomass of mustard, depending on the share of sediment in the substrate (0 to 20 %)

a decrease in nitrogen content in plant biomass on the substratum with 15 % sediment admixture contained the smallest amounts (36.8 g N · kg^{-1} d.m.).

Underwood [8] states 3.0 g P · kg^{-1} as the optimal amount of phosphorus in plants destined for animal feed. Plant material from all treatments of the presented experiment contained approximated to optimal or higher its amounts but twice exceeded average content of this element assessed by Traba et al [7]. The shoots of mustard grown on the control (soil without the sediment) contained the highest amounts of phosphorus (Fig. 2). Small admixtures of the sediment, between 2 and 4 %, had a similar effect on phosphorus accumulation so its content was not changing clearly after these doses application in comparison with the control. Larger doses caused a decrease in phosphorus content and the smallest amounts were assessed in the biomass of plants grown on the substratum with 9 % admixture of bottom sediment (Fig. 2). Lower content of P at over 9 % sediment supplements might have been due to this macroelement dilution in the plant biomass, which production was larger on the substratum with these additions of bottom sediment.

Potassium content in mustard biomass ranged from 7.52 to 47.47 g K $\cdot$ kg^{-1} d.m., with average of 22.07 g K $\cdot$ kg^{-1} d.m. (Table 4, Fig. 2) which in the Authors' own experiment approximated the average assessed by Kozlowski [9] in his research on fodder value of permanent grassland swards. Mustard cultivated in the soil without any admixture contained the highest amounts of potassium. With increasing share of bottom sediment in the substratum, potassium content was decreasing in comparison with the control object. The aboveground biomass of plant which grew on the substratum with a 9 % supplement of bottom sediment contained the least of potassium. Kopec and Gondek [10] state that the right amount of potassium in hay is *ca* 10 g $\cdot$ kg^{-1} d.m. Considering this criterion the obtained average content of this element was over twice higher than optimum. The content most approximate to the optimal was registered when the sediment share in the substratum amounted 15 %. Using criteria proposed by Falkowski et al [6], plants from objects with share of 3–8 % sediment in substratum contained K quantity approximated to optimum.

Calcium content in the aboveground mustard biomass fell within the range of 26.25 to 42.50 g Ca $\cdot$ kg^{-1} d.m., with the average content of 34.08 g Ca $\cdot$ kg^{-1} d.m. (Table 4, Fig. 2) which was about five-fold higher than the average Ca content assessed by Kalembasa and Godlewska [1] in Italian ryegrass on the control object. Even after the application of 1 % sediment supplement calcium content in biomass raised in comparison with the control. Only the 9 % sediment supplement slightly lowered calcium content in plants in comparison with the control. The highest increase in this element content was observed when sediment admixture to the substratum amounted from 4 to 5 %. Independent on sediment addition, plant biomass contained excessive quantity of calcium as compared with optimal value [6].

Magnesium content in mustard aboveground biomass ranged from 2.25 and 5.20 g Mg $\cdot$ kg^{-1} d.m., (Table 4, Fig. 2) and was about twice higher than this element content assessed by Czyz et al [11] and Wojcikowska-Kapusta [12]. On the other hand, Jones and Eck [13] reported that the most frequent magnesium content determined in maize biomass fluctuates from 2.0 to 6.0 g Mg $\cdot$ kg^{-1} d.m. Mg contents assessed in mustard biomass in the Authors' own research were similar. Plants grown in the soil without any admixtures contained the least quantities of magnesium (Fig. 2). Growing share of the sediment in substratum caused an increase of magnesium content in the aboveground biomass of mustard. The weakest effect was observed in plants growing in the substratum with 9 % share of bottom sediment and the strongest one in these cases when its additions amounted 4–5 %. Plant material from all objects contained optimal quantity of magnesium [6].

Sodium contents in mustard shoot biomass ranged from 1.11 to 4.67 g Na $\cdot$ kg^{-1} d.m. with an average of 2.50 g Na $\cdot$ kg^{-1} d.m. (Table 4, Fig. 2). The mean value was about twice higher than this element contents determined by Czyz et al [11] and over five-fold higher than the average assessed in grass mixture by Antonkiewicz [14]. Mustard cultivated in the soil without sediment addition contained 2.06 g Na $\cdot$ kg^{-1} d.m. (Fig. 2).

Admixtures of bottom sediment between 1 and 7 % caused an increase in sodium content in mustard shoot biomass in comparison with the control, which was the biggest when the share of the sediment in the substratum amounted 3 %. Larger admixtures of the sediment decreased sodium content in the plant and when the sediment share in the substratum raised to 8 % and more, gradual decline in this element content was noted in mustard aboveground biomass, below the amount assessed in mustard grown in the soil without supplements. The least quantities of sodium were noted in plants cultivated in the substratum with 20 % share of the sediment. In majority of objects content of sodium was higher than optimal [6].

The highest contents of P, Ca and Mg in plants were noted when the sediment share in the substratum equaled 4 %, whereas the highest N, Na and K values were registered in mustard from the control object and when the sediment share in the substratum was 1 % and 3 %. Large contents of N, Na and K in plants from these objects might have been caused by a higher content of the elements in smaller biomass produced on soil with acid reaction. When soil reaction increase and the plant biomass production is significantly higher mineral elements dilution may be observed. The similar results obtained Niemiec [15] who studied an effect of the same sediment additions to the soil and sand in amounts increasing from 10 to 90 %.

The greatest diversification of the contents was noted for K and Na, whereas P and Mg contents were much less diversified, and the smallest variability was registered for N and Ca (Table 4). The relative standard deviations assumed the following values: 57.9; 47.9; 22.7; 21.5; 15.0 and 6.6 %, respectively.

Conclusions

1. Increasing bottom sediment supplements to the substratum caused increase in yield of the mustard shoot biomass in comparison with that obtained on the control treatment. The best effects were achieved when the sediment share in substratum amounted to 20 %.

2. The contents of studied macroelements in mustard aboveground biomass fell within the following ranges: 36.8–47.1 g N $\cdot$ kg^{-1}; 2.25–5.20 g P $\cdot$ kg^{-1};7.52–47.47 g K $\cdot$ kg^{-1}; 26.25–42.50 g Ca $\cdot$ kg^{-1}; 2.3–4.5 g Mg $\cdot$ kg^{-1} and 1.11–4.67 g Na $\cdot$ kg^{-1} of dry mass.

3. Additions of bottom sediment to the substratum caused a slight decline in N content in mustard biomass as compared with the control. Higher decreases were registered for P and the greatest for K, which content diminished even after the application of the smallest, 1 % or 2 % sediment additions.

4. Bottom sediment supplements to the substratum caused an increase of Ca and Mg content in mustard biomass in comparison with the plants from the control object.

5. Bottom sediment addition amounting to 7 % caused an increase of Na content in mustard shoot biomass, whereas larger supplements lowered this element content in comparison with the control plants.

6. Considering the optimal macrolement content in animal fodder, obtained mustard shoot biomass did not meet the fodder usability criteria on most treatments due to

excessive amount of P, excessive or too low content of K and Na. Biomass from all experimental treatments revealed too high Ca and Mg content.

7. Applied bottom sediment caused soil deacidification and improved plant yielding, so it may be used for improving the properties of light acid soils, but simultaneous control of the plant chemical composition is necessary.

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NASTĘPCZY WPŁYW DODATKU OSADU DENNEGO DO PODŁOŻA NA SKŁAD CHEMICZNY BIOMASY GORCZYCY BIAŁEJ (*Sinapis alba* L.)
CZ. 1. ZAWARTOŚĆ MAKROELEMENTÓW

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem pracy było zbadanie wpływu dodatku osadu dennego do podłoża na skład chemiczny biomasy uprawianych roślin biorąc pod uwagę optymalne zawartości makroelementów w roślinach przeznaczonych na paszę oraz ocena możliwości rolniczego wykorzystania osadu dennego. Materiał do badań stanowiła nadziemna biomasa gorczycy białej (*Sinapis alba* L.), uprawianej w trzecim roku po zastosowaniu osadu dennego bagrowanego ze Zbiornika Rożnowskiego do gleby bardzo lekkiej oraz bardzo kwaśnej. Doświadczenie było kontynuacją badań prowadzonych w latach 2005 i 2006, w których roślinami testowymi były kolejno życica wielokwiatowa (*Lolium multiflorum* L.) i kukurydza (*Zea mays* L.). Udział osadu w podłożu wynosił od 1 do 20%.

Zawartość makroelementów w nadziemnej biomasie gorczycy była zróżnicowana w zależności od udziału osadu dennego w podłożu i mieściły się w zakresach 36,8–47,1 g N, 2,25–5,20 g P, 7,52–47,47 g K, 26,25–42,50 g Ca, 2,3–4,5 g Mg i 1,11–4,67 g Na w 1 kg suchej masy. Spośród badanych pierwiastków najbardziej zróżnicowana była zawartość K (V = 51,85 %) i Na (V = 44,53 %), w znacznie mniejszym stopniu zawartość P (V = 23,27 %) i Mg (V = 19,73 %), a najmniejsze zróżnicowanie zanotowano w przypadku Ca (V = 13,27 %) i N (V = 6,63 %). Największe zawartości P, Ca i Mg zaobserwowano, gdy udział osadu w podłożu wynosił 4 %, a najwięcej N i Na zawierała biomasa gorczycy, gdy udział osadu w podłożu wynosił odpowiednio 1 % i 3 %, a K w roślinach z obiektu kontrolnego. Dodatki osadu dennego do podłoża powodowały zmniejszenie zawartości N, P oraz K, jednocześnie następowało zwiększenie zawartości Ca i Mg w biomasie gorczycy w porównaniu z roślinami z obiektu kontrolnego. Dodatek do 7 % osadu do podłoża powodował wzrost zawartości Na w biomasie gorczycy, a większe dodatki wywołały obniżenie zawartości tego pierwiastka w porównaniu z roślinami wyrosłymi w obiekcie kontrolnym. Uzyskana nadziemna biomasa gorczycy z większości obiektów cechowała się nadmierną zawartością P, Ca i Mg oraz nadmierną lub za małą zawartością K i Na.

Zastosowany osad denny powodował odkwaszanie gleby, oddziaływał pozytywnie na plonowanie roślin, dlatego można go użyć do poprawy właściwości gleb lekkich kwaśnych, jednocześnie jest konieczna kontrola składu chemicznego roślin.

Słowa kluczowe: osad denny, makroelementy, N, P, K, Ca, Mg, Na, zawartość

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Agnieszka BARAN[1] and Czesława JASIEWICZ

ACCUMULATION OF TRACE ELEMENTS IN BLACK AND GREEN TEAS: CHARACTERISTICS OF LEAVES AND BREWS

NAGROMADZENIE PIERWIASTKÓW ŚLADOWYCH W HERBATACH CZARNYCH I ZIELONYCH: CHARAKTERYSTYKA LIŚCI I NAPARÓW

Abstract: The paper aimed to assess the accumulation of trace elements (Fe, Mn, Zn, Cu, Ni, Cr, Pb and Cd) in leaves and brews of black and green teas. Analyzed were total of 17 black teas and 13 green teas. Trace element concentrations in the obtained solutions from leaves and brews were assessed using atomic emission spectrometry in inductively coupled argon plasma (ICP-AES) on JY 238 ULTRACE apparatus (Jobin Von Emission).

Green tea brews contained more valuable elements, such as manganese, iron, zinc, copper, but also more of toxic metals, such as cadmium and lead in comparison with black teas. 18 % of black tea samples and almost 50 % of green tea sampled revealed exceeded admissible lead level. Permissible cadmium level was not exceeded in any tea sample. Green tea brews contained more valuable elements, such as manganese, iron, zinc, copper, but also more of toxic metals, such as cadmium and lead in comparison with black teas. Considering the tested teas, the highest amounts of zinc are extracted from the leaves to the brew (71 % from black teas and 80 % green teas), and the smallest quantities of iron (7 % from black and green teas). Estimated permissible temporary weekly intake (PTWI) of lead and cadmium with four cups of tea is low and fluctuates for lead 8 % and for cadmium over 1 % of PTWI stated in FAO/WHO recommendations.

Keywords: black and green teas, trace elements, leaves, brew, PTWI

Increasing interest in drinking both black and green tea has been observed over the recent years both in Poland and all over the world. Moreover, for many years numerous reports have indicated pro-health properties of tea [1–4]. The research has demonstrated that regular tea drinking prevents neoplastic diseases, diminishes the risk of circulatory diseases, counteracts hypertension and slows down ageing processes. Tea owes its specific taste, aroma and health effect to various components present in its leaves. 300 chemical components have been discovered among them, including a number of

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beneficent elements, eg zinc, copper, iron and manganese. However, progressing environmental pollution may cause the occurrence of excessive amounts of heavy metals eg lead, cadmium or mercury in plant products including teas, which pose a hazard to human health. Because tea drinking is very popular it is most important that these pollutants occur in minimal quantities [3].

The paper aimed to assess the accumulation of trace elements in leaves and brews of black and green teas.

Material and methods

Analyzed were black and green teas. A total of 17 black teas and 13 green ones were tested to determine their concentrations of zinc, copper, manganese, iron, nickel, chromium, lead and cadmium. Ground tea samples were dry-mineralized in quartz crucibles in order to assess trace metal contents in leaves. Obtained ashes were dissolved in 10 % hydrochloric acid. Tea brew was prepared from 2 g weighted portion on which 200 cm^3 boiling water was poured. Tea was brewed for 5 minutes. Trace element concentrations in the obtained solutions from leaves and brews were assessed using *atomic emission spectrometry in inductively coupled argon plasma* (ICP-AES) on JY 238 ULTRACE apparatus (Jobin Von Emission). Beside the contents of analyzed trace elements, also their daily uptake by an adult human organism consuming four cups of tea was computed. The uptake was computed as a product of the element content in brews and daily tea consumption [5, 6].

Obtained results were elaborated statistically using one-way ANOVA and LSD test. The analysis of variance was conducted at the significance level $\alpha = 0.05$. Moreover, arithmetic mean, *standard deviation* (SD), median and coefficient of variance (V %) were computed. The results were elaborated using Statistica 9.0 programme.

Results and discussion

Trace elements in tea leaves

The analyzed black and green teas differed with their contents of trace elements, however only copper, manganese and iron content was statistically significant diversified (Table 1).

Green teas revealed over 1-fold higher level of manganese, 2-fold higher level of iron and over 1-fold lower level of copper than black teas. The contents of elements in tea leaves may be arranged as follows: manganese > iron > zinc > cooper > nickel > chromium > lead > cadmium. From among the analyzed elements, chromium contents in teas revealed the greatest diversification (V = 104 % in black teas and V = 138 % in green teas), on the other hand zinc content was the least diversified in black teas (V = 21 %) and copper in green teas (V = 16 %) (Table 1).

A slight difference was registered in zinc content between black and green teas. Zinc level in teas ranged from 13.3 and 87.4 $mg \cdot kg^{-1}$ d.m. (Table 1). Among black teas, the highest zinc contents were noted in *Lipton Earl Grey Tea* and among green teas in *Sir*

Roger Ekologiczna, whereas the lowest in black tea *Dilmach Yatta Wate* and in green tea *Lipton Mystic Nepal*. Gajewska et al [2] found a similar range of zinc contents in teas. According to Falandysz and Kostecka [7] zinc contents in black teas are much higher and range from 30 to 50 mg Zn $\cdot$ kg^{-1} d.m.

Table 1

Trace elements content in leaves black and green teas [mg $\cdot$ kg^{-1} d.m.]

Metal	Tea	Mean	Median	Range	V [%][a]	$LSD_{0.05}$
Zn	Black Green	26.51 ± *5.85* 27.80 ± *8.44*	17.80 25.65	17.8–87.4 13.3–56.4	21 32	n.s.[b]
Cu	Black Green	18.35 ± *4.45* 15.02 ± *2.36*	18.75 14.30	10.0–28.4 10.70–19.8	24 16	7.05
Mn	Black Green	678.79 ± *303* 909.28 ± *293*	597.5 896.0	303.0–1340.0 572.0–1690	51 32	596.22
Fe	Black Green	151.18 ± *78.2* 311.73 ± *161*	118.5 232.0	58.9–364.0 163.0–1110	45 19	389.96
Ni	Black Green	4.91 ± *1.73* 4.24 ± *1.45*	4.54 4.37	2.28–10.69 1.68–6.83	35 34	n.s.
Cr	Black Green	1.19 ± *1.24* 1.12 ± *1.55*	0.82 0.54	0.27–7.37 0.22–5.64	104 138	n.s.
Pb	Black Green	0.78 ± *0.60* 0.93 ± *1.00*	0.56 0.54	0.21–2.49 0.01–3.32	77 107	n.s.
Cd	Black Green	0.03 ± *0.02* 0.04 ± *0.02*	0.03 0.04	0–0.07 0.01–0.24	69 51	n.s.

[a] Variability coefficient; [2] no significant.

Copper contents in teas fluctuated from 10.0 to 28.4 mg Cu $\cdot$ kg^{-1} d.m. (black teas) and from 10.70 to 19.8 mg Cu $\cdot$ kg^{-1} d.m. (green teas). Maximum copper levels were revealed in black tea *Bastek Madras* and in *Sir Roger* green tea, whereas the minimum in *Cycur-Turcja* black tea and *Malwa Zielona z Imbirem* green tea. In research conducted by Gajewska et al [2] copper contents in black and green teas were on average 1.5-fold higher in comparison with our results, respectively 31.3 mg (black teas) and 20 mg Cu $\cdot$ kg^{-1} d.m. (green teas).

Manganese concentrations in the analyzed teas ranged from 303.0 to 1690 mg Mn $\cdot$ kg^{-1} d.m. Maximum manganese levels were assessed in *Vitax* green tea (1690 mg $\cdot$ kg^{-1} d.m.) and in *Bastek Madras* black tea (1310.0 mg $\cdot$ kg^{-1} d.m.). On the other hand the lowest manganese contents were assessed in *Twinnings of London* black tea (303.0 mg $\cdot$ kg^{-1} d.m.) and in *Lipton Mystic Nepal* green tea (572.0 mg $\cdot$ kg^{-1} d.m.). Gajewska et al [2000] revealed slightly lower concentrations on manganese in green teas between 363 to 961 mg Mn $\cdot$ kg^{-1} d.m. at average of 663 mg Mn $\cdot$ kg^{-1} d.m. On the other hand in black teas the author assessed average manganese content amounting to 788 mg Mn $\cdot$ kg^{-1} d.m., which corresponded with the reported results. Investigations conducted by other authors revealed in black teas between 413 and 1124 mg Mn [8], from 410 to 1200 mg Mn [7, 8] and on average 690 mg Mn $\cdot$ kg^{-1} d.m. [10]. Higher contents of manganese in black teas, on average 1867 mg Mn · kg^{-1} d.m., were registered by Ozdemiri and Gucer [11], whereas in green teas Chu and Juneja [12] noted from 500 to 3000 mg Mn · kg^{-1} d.m.

Iron content in teas was on the level from 58.9 to 1110.0 mg · kg^{-1} d.m. Green teas contained over two-fold higher quantities of this element than black ones. The highest iron concentrations among black teas were assessed in *Bastek Madras* (337.50 mg Fe · kg^{-1} d.m.) and among green teas in *Bastek* (1110.0 mg Fe · kg^{-1} d.m.). The lowest iron content (58.9 mg Fe · kg^{-1} d.m.) was registered in *Ahmad Tea Assam* black tea and in *Posti* green tea (163.0 mg Fe · kg^{-1} d.m.). Higher iron concentrations in black teas in comparison with green ones were assessed in the investigations of Gajewska et al [2]. Black teas contained on average 550 mg Fe · kg^{-1} d.m. and green ones 216 mg Fe · kg^{-1} d.m. [2].

Nickel contents in teas ranged from 1.68 to 10.69 mg · kg^{-1} d.m. Black and green teas showed a similar level of nickel. Maximum nickel contents (10.69 mg · kg^{-1} d.m.) were assessed in *Black Madras* black tea and in *Sir Roger* green tea (6.83 mg · kg^{-1} d.m.). Minimum levels of this metal (2.28 mg · kg^{-1} d.m.) were determined in *Dilmah Yatta Wate* black tea and in *Lipton Mystic Nepal* green one (1.68 mg · kg^{-1} d.m.). Similar nickel contents in black teas, between 2.98 and 9.29 mg Ni · kg^{-1} d.m., were registered in the investigations of Bulinski and Bloniarz [8]. In the work by Gajewska et al [2] black and green teas had about twice higher concentrations of this metal, 8.2 and 7.7 mg · kg^{-1} d.m. respectively.

Similar as nickel, mean chromium contents in black and green teas were approximate. Black teas contained on average 1.19 and green 1.12 mg Cr · kg^{-1} d.m. The highest chromium content (7.37 mg · kg^{-1} d.m.) was registered in *Irving Daily Classic* black tea and in *Posti* green tea (5.64 mg · kg^{-1} d.m.), on the other hand the lowest chromium concentration (0.27 mg · kg^{-1} d.m.) was assessed in *Dilmah Yatta Wate* black tea and in *Lipton Mystic Nepal* green tea (0.22 mg · kg^{-1} d.m.). Gajewska et al [2] registered on average 1.25 mg Cr in black teas and 1.35 mg · kg^{-1} d.m. in green teas.

Lead contents in black teas fluctuated from 0.21 to 2.49 mg · kg^{-1} d.m. while in green teas from 0.01 to 3.32 mg · kg^{-1} d.m. The greatest content of lead was assessed in *Bastek Madras* (black teas) and in *Richmond Hill* (green teas).The lowest levels were noted in *Irving Daily Classic* black and in *Sen-Cha USA* green tea. As has been shown in Table 1, average levels of lead in both kinds of tea were approximate, however slightly higher amounts of this metal were assessed in green than in black teas. In the research conducted by Gajewska et al [2] in green tea leaves lead contents were registered from 0.37 to 6.2 mg Pb · kg^{-1}, on average of 2.68 mg Pb · kg^{-1} d.m., while in black teas between 0.55 and 6.9 mg Pb, on average of 2.63 mg Pb · kg^{-1} d.m.

Average cadmium content in black teas was on the level of 0.03 mg, whereas in green teas 0.04 mg Cd · kg^{-1} d.m. Trace amounts of cadmium were assessed in *Oskar Black Tea*, *Lipton Gold Tea* and *Dilmah Yatta Wate* (black teas) and in *Malwa Zielona z Imbirem* (green tea). Maximum contents of this metal were found in *Twinnings of London* (black tea) and *Teekane* (green tea). Obtained results are congruent with the research conducted by Bulonski and Bloniarz [1] and Sedrowicz et al [10]. On the other hand Gajewska [2] assessed over 14-fold higher amounts of cadmium in black teas and over 5-fold higher in green teas in comparison with the presented results.

Trace element contents in black and green teas were assessed on the basis of the Regulation of the Minister of Health dated 13.01.2003 on maximum levels of chemical and biological pollutants in food, food components, permissible additives, substance enhancing processing or on food surface [13]. In pursuance of the above-mentioned regulation permissible contents of lead and cadmium in teas should not exceed 1 mg Pb and 0.1 mg Cd $\cdot$ kg^{-1} d.m. Considering the above stated norm, none of the tested tea samples exceeded the permissible levels of cadmium. As shown by the tests, permissible limit of lead was exceeded in 18 % of black tea samples and in almost 50 % of green teas. Exceeding the admissible norm for lead was demonstrated for green teas: *Teekane, Sir Roger, Bastek, Tesco Green Tea, Malwa Zielona z Imbirem* and *Canadian Richmond Hill*. Green tea labeled "organic" deserves particular attention. Although the admissible norm of cadmium established by the Minister of Health [13] was not exceeded in it, yet the level of this metal assessed in it was among the highest registered in green teas, ie 0.07 mg $\cdot$ kg^{-1} d.m. Exceeded admissible amount of lead was also noted in this tea, since 1.39 mg Pb $\cdot$ kg^{-1} d.m. was assessed in it. It may be supposed that lead is easily extracted from the leaf tissue but may also originate from pollutants deposited on the external parts of tea bushes, which may be cultivated in the region where the metal concentrations in the air are elevated.

Assessment of the capability of trace element release from tea leaves: brews

Teas are usually consumed as water brew, therefore it is necessary to determine the degree of element passing from the leaves to the brew (Fig. 1).

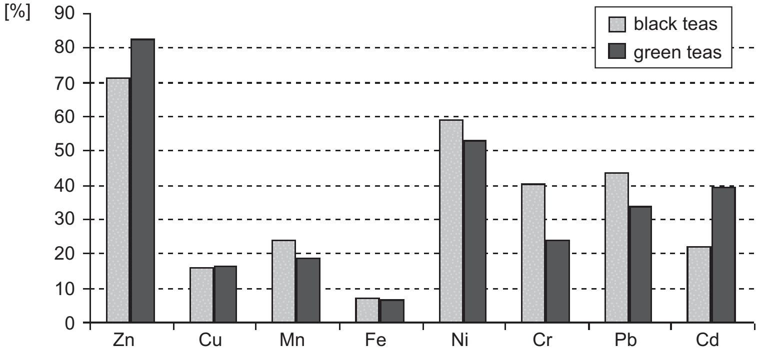

Fig. 1. Percentage extraction of heavy metals from the leaves of black and green tea to infusions

The time of tea brewing in the presented experiment was 10 minutes and might have influenced the amount of metals extracted from the leaves to the brew. In the experiment conducted by Sedrowicz et al [10] it was found that after 30 minutes of brewing the amounts of most metals diminish in the brews in comparison with maximum values observed in the 2nd minute for Pb, in the 5th minute for Mn and Cu, in the 10th minute for Zn and in the 20th minute for Cd and Ni. Therefore, it may be supposed that metal concentrations in tea depend on the time of brewing. Research has demonstrated that the largest amounts of zinc and the smallest of iron pass from tea leaves to the brew. Over 71 % of zinc, 50 % of nickel, 40 % of chromium and lead, 22 % of cadmium and manganese, 16 % of copper and 7 % of iron pass from black tea leaves to the brew. On the other hand, from green tea leaves 80 % of nickel, 52 % of lead and cadmium 34 % and 39 % of chromium, manganese and copper, respectively 24 %, 19 % and 16 % and 7 % of iron were extracted from the leaves to the brew. A comparison of the results with the research conducted by other authors [1, 2, 8, 9, 14] revealed a considerably higher degree of zinc, cadmium and lead passing from the leaves to the tea brews; the degree was lower for copper and manganese but comparable for iron. Gajewska et al [2] demonstrated the average percent of extraction for zinc 32 % and 31 %, for lead 31 % and 23 %, for cadmium 15 % and 12.5 %, for copper 23 % and 22 %, for manganese 29 % and 31 % and for iron 3.5 % and 6 % from black and green teas, respectively.

The element present in the highest quantities in the analyzed teas was manganese. Consuming tea brew, particularly green tea, which is more abundant in manganese than black tea increases the amount of this microelement in human diet. It was estimated that soluble manganese forms constituted on average 23%, whereas in the investigations of Buliński and Błoniarz [8], the extraction degree was 20%. Falandysz and Kostecka [9] noted that efficiency of manganese leaching from dry teas to water phase depended on the way and duration time of tea brewing but was not connected with the tea dry mass used for brew preparation.

Absorption of trace elements

Moreover, it should be emphasized that registered element levels supply to our diet some determined doses of desired elements which are very important for the proper functioning of human organism (Table 2). Also, while considering the problem of passing of toxic metals, such as cadmium or lead to the brews (between 22 and 40 %) and assuming daily drinking of 4 cups of tea, it is obvious that small amounts of metals are supplied to the organism, fluctuating from 8 % of lead and over 1 % of cadmium *permissible temporary weekly intake* (PTWI) stated in the FAO/WHO recommendations (Table 2) [5, 6].

Table 2

Daily and weekly intake of elements in drinking 4 cups of tea

Tea	Zn	Cu	Ni	Cd	Pb	Cr	Mn	Fe
[mg · kg^{-1} · day^{-1}]								
Black	0.22	0.02	0.02	0.0001	0.002	0.002	1.24	0.07
Green	0.76	0.02	0.02	—	0.002	0.001	1.36	0.11
[mg · kg^{-1} · week^{-1}]								
Black	1.54	0.14	0.14	0.0007	0.014	0.014	8.68	0.49
Green	5.32	0.14	0.14	—	0.014	0.007	9.52	0.77

PTWI of lead – 0,025 mg · kg^{-1} b.m. (*body mass*), of cadmium – 0,007 mg · kg^{-1} b.m.

Conclusions

1. 18 % of black tea samples and almost 50 % of green tea sampled revealed exceeded admissible lead level. Permissible cadmium level was not exceeded in any tea sample.

2. Green tea brews contained more valuable elements, such as manganese, iron, zinc, copper, but also more of toxic metals, such as cadmium and lead in comparison with black teas.

3. Considering the tested teas, the highest amounts of zinc are extracted from the leaves to the brew (71 % from black teas and 80 % green teas), and the smallest quantities of iron (7 % from black and green teas).

4. Estimated permissible temporary weekly intake (PTWI) of lead and cadmium with four cups of tea is low and fluctuates for lead 8 % and for cadmium over 1 % of PTWI stated in FAO/WHO recommendations.

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NAGROMADZENIE PIERWIASTKÓW ŚLADOWYCH W HERBATACH CZARNYCH I ZIELONYCH: CHARAKTERYSTYKA LIŚCI I NAPARÓW

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Abstrakt: Celem pracy była ocena zawartości pierwiastków śladowych (Fe, Mn, Zn, Cu, Ni, Cr, Pb oraz Cd) w liściach i naparach herbat czarnych i zielonych. Badaniom poddano 17 próbek herbat czarnych i 13 zielonych. Zawartość pierwiastków w liściach i naparach oznaczono po suchej mineralizacji metodą ICP-EAS.

Herbaty zielone zawierały więcej cennych pierwiastków, takich jak mangan, żelazo, cynk, ale także więcej metali toksycznych, takich jak kadm i ołów. W 18 % próbek herbat czarnych i blisko 50 % próbek herbat zielonych miało przekroczony dopuszczalny limit ołowiu. Dopuszczalny poziom kadmu w żadnej herbacie nie był przekroczony. Z badanych herbat najwięcej z liści do naparu ekstrahowało się cynku (71 % herbaty czarne i 80 % herbaty zielone), a najmniejsze żelaza (7 % herbaty czarne i zielone). Oszacowane *tymczasowe dopuszczalne tygodniowe pobrania* (TDTP) ołowiu i kadmu z wypiciem 4 filiżanek herbaty, jest małe i wynosi w przypadku ołowiu 8 % i dla kadmu ponad 1 % PTWI podanego w zaleceniach FAO/WHO.

Słowa kluczowe: herbaty czarne, zielone, pierwiastki śladowe, liście, napary, TDTP

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APLICATION OF HEAVY METALS AND NUTRIENTS INTO NATURAL ENVIRONMENT WITH SEWAGE SLUDGE

METALE CIĘŻKIE I SKŁADNIKI POKARMOWE WPROWADZANE DO ŚRODOWISKA PRZYRODNICZEGO Z OSADAMI ŚCIEKOWYMI

Abstract: The paper presents results of examinations of sludge from dairy sewage treatment plants in north-eastern Poland and results of examinations of compost obtained from research facilities applying low-expenditure methods of treatment of dairy sewage sludge with added structural materials. Chemical substances have been analyzed and their amount estimated, together with diary sewage sludge entering the environment. Admissible amounts of heavy metals contained in sewage sludge according to Polish and international legal regulations have been referred to.

Very low harmfulness of diary sludge has been stated. It has been demonstrated that the process of composting and vermicomposting has changed the structure of the sludge and additionally enriched it with fertilizer values (N, P, K content) and soil formation values.

Keywords: vermiculture, sewage sludge, low cost methods, compost, vermicompost, Dairy Industries

Sludge is the source of mineral and organic pollution. In recent years much attention has been paid to examining organic pollution. In sewage sludge 516 compounds have been identified and classified into 15 classes. Among them are *polycyclic aromatic hydrocarbons* (PAHs), *adsorbable organic halogens* (AOX), *polychlorinated biphenyls* (PCBs), and others. Besides these compounds, in sewage sludge can be found toxic trace elements which hamper sludge utilization. Sludge is also a source of organic matter, as well as macro- and microelements of agricultural significance, hence it can be applied in agriculture [1].

In the north-eastern part of Poland, sludge is more and more widely managed and exposed to low-expenditure treatment methods. Such activities have been influenced by the following factors: agricultural and industrial specificity of the region, sludge

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characteristics, biomass in form of straw, sawdust and chips present in the Green Lungs of Poland Region, soils of low class, and bigger amount of small and medium sewage treatment plants [2].

At present, in Podlasie province there are 113 municipal and 30 industrial sewage treatment plants of throughtput of several to several thousand cubic meters per day [3]. In the 1990's a significant progress was observed in the field of protection of water environment of the region. Many new facilities were constructed, capable of intense sewage treatment. Most serious negligence concerns industrial sewage treatment, in particular dairy workshops. Most new and modernized sewage treatment plants marginalized the problem of sewage sludge treatment by applying natural or mechanical appliances for sludge dewatering. Because of physical and chemical composition of sewage sludge from dairy industry, it should be considered as a raw material rather than waste. The fundamental criterion enabling sludge return to the natural environment is its sanitary condition. The author's research shows that dairy industry sludge basically does not contain pathogenic organisms, including bacteria, fungi, protozoa, parasites and their fertilized eggs, which would prevent their use for non-industrial purposes. Moreover, the sludge is characterized by very low content of heavy metals and other specific chemical compounds (very often present in municipal sewage sludge) as well as high fertilizing values; it is the source of carbon as well as nitrogen and phosphorus. At the same time, the waste is very often considerably liquefied, which makes its thorough distribution on the ground difficult. Safe application of the sludge in the environment without prior treatment becomes more and more limited because of legal regulations which limit, and in the nearest future will prevent, direct fertilizing application of untreated sewage sludge. On the other hand, soil structure of Poland and its north-eastern regions is dominated by light soils which are characterized by low content of nutrients, poorly developed sorptive complex, and an inconsiderable amount of humus. Entry to soils of fertilizer in form of treated sewage sludge from dairy industry and composts obtained with participation of other components should be considered as a factor which counteracts soil degradation and enhances soil fertility [2, 4].

Material and methods

The article presents results of examinations of dairy sewage sludge in north-eastern Poland and results of examination of composts obtained from research facilities applying low-expenditure methods of treatment of dairy sewage sludge with added structural material.

The purpose of the examinations was to analyze and estimate chosen chemical pollutants entering the environment together with stabilized sewage sludge from dairy sewage treatment plants and treated by means of low-expenditure methods. The general concept of the examinations assumed comparing obtained results of examinations of the sludge with added components from chosen facilities treating sludge with the use of California earthworm and in the process of windrow composting. Obtained results included examinations carried out in dairy sewage treatment plants and in research facilities located in Rudka forest inspectorate and in a sewage treatment plant in Zambrow.

Examinations were carried out in research facility in technological scale in Rudka forest inspectorate in Korycin tree nursery where sewage sludge was composted in windrow composting technology with throwing of compost by means of a compactor. Basic structural materials used in the process of composting in the facility were sawdust, straw and chips. Another research facility in technological scale is located in a sewage treatment plant in Zambrow where sewage sludge is treated with the use of vermiculture. Beds with vermiculture were fed with the same dairy sewage sludge with liquefication of approx. 80 %, once, in the amount of 1.5 m^3 of liquefied sludge per bed of 4 m^2. Before being fed, the bed was embanked with the so-called lair of California earthworms (*Eisenia fetida*) coming from the sewage treatment plant in Zambrow. Earthworms consume sludge and excrete coprolites, ie vermicompost. Both facilities used stabilized sewage sludge from dairy sewage treatment plant of S.M. MLEKOVITA in Wysokie Mazowieckie [1, 5].

The analysis of obtained material included the following examinations: heavy metal content, fertilizing values, liquefication, dry mass, and reaction. The examinations were carried out in the Department of Technology in Engineering and Environmental Protection laboratory according to valid norms.

Sludge samples were treated with mineralization in HACH mineralizator with the use of sulphuric acid and hydrogen peroxide in mixture of nitric and hydrochloric acid in ratio 1:3. For further analysis mineralizats were filtered through MN 616 G paper filter.

Determination of cadmium, nickel and total chromium content was done in samples of mineralizats with the use of *atomic absorption spectrometr* Perkin-Elmer 4100 ZL with transversely heated graphite cuvette and Zeeman-effect background correction.

Determination of mercury content was done in samples of mineralizats by means of cold steam technique with the use of atomic absorption spectrometr Perkin-Elmer 4100 ZL equipped in add-on device FIAS-200.

Determination of zinc, lead and copper content was done in samples of mineralizats by means of flame atomization, and potassium content was done by means of *atomic emission spectroscopy* (AES) with the use of atomic emission spectrometr Varian SpectrAA 20 Plus.

Fig. 1. Flow diagram of the research installation

Results and discussion

In the last decade, the amount of sewage sludge generated by the analyzed dairy sewage treatment plants increased considerably, and presently it amounts to approx. 3450 Mg of dry mass per year. In comparison, all municipal sewage treatment plants in the province produced 17409 Mg of sludge dry mass, out of which 6865 Mg of dry mass were applied in agriculture or for remediation. In 2009, global amount of sludge from industrial sewage treatment and pretreatment plants amounted to 7360 Mg, out of which 3550 Mg of dry mass were applied in agriculture or for remediation [3]. It implies that in the province approx. 40 % of municipal sludge and nearly 50 % of sewage sludge was environmentally applied. Thus, dairy sludge constitutes approx. 47 % of industrial sludge in the province and is environmentally used in almost 100 %. There was an increase of approx. 150 % in the amount of dairy sludge comparing with the amount in the mid 1990's.

Dairy sewage sludge is characterized by much lower heavy metal content than municipal sludge. Table 1 presents average amounts of heavy metals in stabilized sewage sludge from diary workshops in the region in the last 10 years, and composts obtained from sludge from the largest facility in Wysokie Mazowieckie.

Table 1

Heavy metals content in sewage sludge from dairy wastewater treatment plants (average values 2000–2009) and compost from Rudka Forestry research installation and Zambrow instalation

Localization	The quantity of heavy metals [mg · kg^{-1} d.m.]						
	Pb	Zn	Cu	Cd	Ni	Cr	Hg
Sejny	10.0	240	26	0.80	1.9	2.1	0.17
Bielsk Podlaski	5.0	348	24	0.42	12.1	13.1	0.11
Zambrow	8.1	230	28	0.92	9.1	9.6	0.23
Wysokie Mazowieckie	12.0	366	45	0.52	5.1	18.4	0.20
Grajewo	19.9	327	22	0.45	7.4	17.6	0.19
Monki	4.2	197	31	0.11	6.8	11.5	0.21
Kolno	12.6	139	17	0.15	8.0	6.9	0.06
Piatnica	7.1	410	15	0.26	7.9	14.8	0.10
Rudka (compost)	7.8	149	23	0.48	4.9	6.3	0.15
Zambrow (vermicompost)	6.2	195	22	0.34	3.8	7.9	0.14

Source: own data processing [1, 6].

Table 2 presents basic fertilizing values of sewage sludge from analyzed dairy sewage treatment plants.

All dairy sludge are characterized by high fertilizing value. Also characteristic is very high content of nitrogen and phosphorus compounds as well as organic substance. Most facilities do not apply the process of hygienization because of very good sanitary condition of the sludge. In order to obtain proper parameters of biomass exposed to the process of composting, according to assumed methodology and technology, dewatered

Table 2

Basic fertilizing values of sewage sludge from dairy wastewater treatment plants – average values 2000–2009

Localization	Chosen fertilizing parameters						
	Total N	Ammonia N	Total P	Magnesium	Calcium	Organic substance	pH
	[g · kg^{-1} d.m.]					[%]	
Sejny	69.2	2.8	69.1	5.2	17.5	61.2	7.32
Bielsk Podlaski	21.6	2.6	21.6	6.8	61.9	74.2	7.67
Zambrow	93.5	0.5	48.8	5.7	41.3	74.0	7.13
Wysokie Mazowieckie	92.6	2.9	22.5	3.9	28.2	82.9	12.71
Grajewo	34.9	11.5	10.6	1.0	24.9	67.1	7.19
Monki	62.5	6.4	64.0	2.1	18.0	64.3	6.64
Kolno	71.1	1.8	71.0	5.8	49.0	34.1	7.21
Piatnica	74.3	38.0	7.6	6.9	12.4	82.0	7.33

Source: own data processing.

dairy sewage sludge have been mixed with various structural materials. Table 3 presents heavy metal contents in materials mixed with sludge. Amounts of individual metals are very low.

Table 3

Heavy metals contents in origin material

Substrate	Pb	Hg	Cu	Cd	Ni	Zn	Cr
	[mg · kg^{-1} d.m.]						
Straw	9.0	0.018	10.0	0.18	4.5	20.0	4.0
Saw dust	10.0	0.06	4.8	0.20	5.0	12.5	2.3
Wooden chip	25.0	0.14	18.0	0.80	6.0	118	12.0

Source: [1].

Examinations of applied structural materials for biogenic elements and macroelements (Table 4) show, first of all, very high carbon content: 35 % to 44.5 %. Thus, it is a material which is supposed to regulate proportion C:N in compost mass. Content of the remaining components is less important regarding their content in dairy sludge.

Table 4

Origin material – fertilizing values

Parameter	Unit	Substrate		
		straw	saw dust	wooden chip
Ca	[g · kg^{-1} d.m.]	6.6	6.7	2.9
	[% CaO d.m.]	0.92	0.94	0.4

Table 4 contd.

Parameter	Unit	Substrate		
		straw	saw dust	wooden chip
Mg	[g · kg^{-1} d.m.]	0.6	0.63	0.55
	[% MgO d.m.]	0.10	0.10	0.09
Total N	[g · kg^{-1} d.m.]	7.14	4.28	12.3
	[% d.m.]	0.71	0.43	1.23
Ammonia N	[g · kg^{-1} d.m.]	0.61	1.30	0.80
	[% d.m.]	0.061	0.13	0.08
Total P	[g · kg^{-1} d.m.]	5.36	1.85	1.43
	% P_2O_5 d.m.	2.46	0.85	0.65
K	[g · kg^{-1} d.m.]	5.2	0.5	3.9
TOC*	[g · kg^{-1} d.m.]	375.9	444.6	350.4
	[% d.m.]	37.6	44.5	35.0

* Total Organic Carbon.
Source: [1]

Tables 5 and 6 present legal regulations in Poland and other countries concerning permissible concentration of heavy metals entering the environment together with sewage sludge during its agricultural application.

Table 5

Permissible heavy metals content [mg · kg^{-1} d.m.] in sewage sludge for agriculture disposal

Metals	Poland	UE directive	Denmark	Austria	Germany	Switzer-land	Sweden	USA
Pb	750	750	120	500	900	500	100	840
Cd	20	20	0.8	10	10	5	2	85
Cr	500	1000	100	500	900	500	100	3000
Cu	1000	1000	1000	500	800	600	600	4300
Ni	300	300	30	100	200	80	50	420
Hg	16	16	0.8	10	8	5	25	57
Zn	2500	2500	4000	2000	2500	2000	800	7500

Source: own data processing [7–9].

Working document on sludge. 3rd Draft. Brussels, 27 April 2000 – a document presenting significant tightening of quality expectations and limitations in agricultural application of sludge. Detailed plans were to decrease total amount of potentially dangerous substances and elements [10]. Council Directive 86/278/EEC of June 1986 on protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, was replaced with Council Directive 91/962/EWG and Council Regulation 807/2003/WE (Dz. Urz. WE L 181 from 04.07.1986, page 6, with later changes). At present, European Commission is elaborating on "Working document sludge and biowaste” 21st September 2010, Brussels, in which same changes in Sewage sludge Directive are suggested.

Table 6 presents permissible heavy metal content in sludge applied in agriculture.

Table 6

EU heavy metals limits in sewage sludge applied in agriculture

Metal	Heavy metals limits [mg · kg^{-1} d.m.]		
	1986/278/EWG	Working dokument on sludge. 3rd Draft	Working document sludge and biowaste 21 September 2010, Brussels
Cd	20–40	10	10
Cr	—	1000	1000
Cu	1000–1750	1000	1000
Hg	16–25	10	10
Ni	300–400	300	300
Pb	750–1200	750	500
Zn	2500–4000	2500	2500

Source: [10–12].

Analysis of Tables 5 and 6 points out a few important changes in regulations concerning sludge agricultural application in Poland and other countries of EU. Update of Sewage Sludge Regulation in 2010 has changed mostly attitude to the issue of heavy metals doses entering the environment. Maximal content of heavy metals in sewage sludge and admissible levels of sludge doses allowed within year per hectare were defined.

Suggested changes relate to:

– Requirements for pollutants prevention,

– Sewage sludge treatment and application as well as conditions of its agricultural application.

Changes regarding sewage sludge utilization on soil are as follow:

– Implementation of stricter solution for heavy metals,

– Standards determination for organic compounds and pathogenic organisms,

– Higher requirements concerning sewage sludge application, sampling and monitoring.

Planned changes in Sewage Sludge Directive do not consider:

– Implementation of strict standards for all substances and prohibition of sludge application on some crops, for the reason of too high costs,

– Prohibition of sludge application on soil.

Changes in Sewage Sludge Directive drive to reduction of dangerous organic substances and heavy metals in sewage discharged to sewerage, which enter sewage sludge. Regulation changes in the range of sewage sludge concern implementation of sewage sludge producer responsibility, certification and requirement applied information for produces and sludge receiver.

Conclusions

Analysis of presented results unequivocally shows low content of heavy metals entering the environment as a result of agricultural application of sludge from dairy sewage treatment. Discovered amounts of heavy metals in the sludge are very often several or a few hundred times lower than permissible ones according to various documents and legal acts in Poland and worldwide. At the same time examinations have shown very low content of heavy metals in structural materials applied during the process of windrow composting or with the use of California earthworm (*Eisenia fetida*) [13, 14]. Adding structural materials has positively influenced these characteristics of treated sludge which are significant in environmental application. The process of composting and vermicomposting has changed sludge structure and additionally enriched it with fertilizer values (N, P, K content) and soil formation values (eg humification and mineralization process).

These are technologies which enrich sewage sludge by causing quick fading of putrid smell, formation of permanent crumb texture which enhances plant growth or increase in level of nutrients on utilized base [15–17].

Examined sludge from sewage treatment plant in Wysokie Mazowieckie fulfills basic criteria and can be used untreated for agricultural and non-agricultural purposes and for soil remediation.

Until now, Polish research on agricultural application of sewage sludge has not attempted to test properly prepared dairy sludge. However, managing sludge from dairy sewage treatment plants in large production facilities is highly problematic. Different character and physical and chemical composition of dairy sludge in comparison with typical municipal sludge (among others much higher nitrogen and phosphorus content in sludge in relation to carbon compounds, and presence of large amounts of coagulated protein) are the reason why technological methods and parameters of sludge treatment developed for municipal sewage sludge, eg into compost, do not bring the desired effects [18, 19]. At the same time, according to Waste Management Act sludge from dairy sewage treatment plants is considered as municipal sewage sludge [20].

Both Polish and international examinations of production of compost, vermicompost, remediation measures, and natural fertilizers mostly concern municipal sludge of different chemistry and character than dairy sludge.

1. Suggested legislative changes in Poland and EU concerning environmental sewage sludge application prefer application of sewage sludge with low heavy metals content and high nutrient values, as well as sanitary safe. Research has demonstrated that sludge from dairy sewage treatment plants meet these requirements.
2. Sludge from dairy sewage treatment plants, which constitutes 40 % of sewage sludge generated in Podlasie province, can be significant source of nutrients in soil.
3. Composting process of the sludge from dairy sewage treatment plants increases its value for agricultural application.

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METALE CIĘŻKIE I SKŁADNIKI POKARMOWE WPROWADZANE DO ŚRODOWISKA PRZYRODNICZEGO Z OSADAMI ŚCIEKOWYMI

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Politechnika Białostocka

Abstrakt: W artykule przedstawiono wyniki badań osadów z oczyszczalni ścieków mleczarskich w północno-wschodniej Polsce oraz wyniki badań kompostów uzyskanych w instalacjach badawczych stosujących niskonakładowe metody przetwarzania osadów ściekowych mleczarskich oraz dodawanych do tych osadów materiałów strukturotwórczych. Dokonano analizy substancji chemicznych i oceny ich ilości z wprowadzanymi do środowiska osadami mleczarskimi. Odniesiono się do ilości dopuszczalnych metali ciężkich zawartych w osadach w prawodawstwie polskim i w innych krajach. Stwierdzono bardzo małą szkodliwość osadów mleczarskich. Wykazano, że proces kompostowania i wermikompostowania zmienił strukturę osadu, a także wzbogacił dodatkowo o wartości nawozowe (zawartość N, P, K) i glebotwórcze.

Słowa kluczowe: wermikultura, osady ściekowe, niskonakładowe metody, kompost, wermikompost, przemysł mleczarski

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REMOVAL OF ORGANIC AND BIOGENIC COMPOUNDS FROM REJECT WATER WITH CONSTRUCTED WETLANDS

USUWANIE SUBSTANCJI ORGANICZNEJ ORAZ ZWIĄZKÓW BIOGENNYCH Z ODCIEKÓW METODĄ HYDROFITOWĄ

Abstract: There are 16 dairy processing plants operating in Podlasie region, including 9 that use individual systems for sewage treatment, while others dispose wastewaters to municipal wastewater treatment plants. Personal Equivalent (P.E.) for individual objects ranges from 7000 to almost 240000 at the flow rate from 500 up to 5240 m^3 of sewage daily. Most of objects were built in 70's of the 20th century; they are overloaded due to the increase of production in factories and works observed for over 20 years. The increase of sewage load made also the increase of sewage sludge and reject water amounts. Reject water is in general directed to the beginning of the treatment process, which is a considerable load, namely due to ammonium nitrogen form. Applying the separate reject water treatment using constructed wetland is one of the possibilities to lower the dairy sewage treatment plant loads. The method can be an alternative for advanced and expensive technologies for purifying the reject waters from treatment plants that use anaerobic sludge stabilization. Studies were carried out in August–October 2008 in research installation designed by the author and operating in dairy sewage treatment plant in Bielsk Podlaski.

Reject waters generated in sewage sludge thickening chamber were subject to purification. Mean pollutants concentrations in reject water were: BOD_5 – 118.6 mg $O_2 \cdot dm^{-3}$, COD – 242.1 mg $O_2 \cdot dm^{-3}$, Kjeldahl's nitrogen – 17.2 mg $N_{TKN} \cdot dm^{-3}$, ammonium nitrogen – 10.4 mg $N \cdot dm^{-3}$, and total phosphorus – 7.2 mg $P_T \cdot dm^{-3}$. BOD_5 removal efficiency was 69.4 %, COD 53.7 %, Kjeldahl's nitrogen 55.8 %, ammonium nitrogen 72.1 %, and total phosphorus 19.4 %, on average. Mean effect of organic substance removal measured as BOD_5 was achieved at the level of 20.6 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$, while ammonium nitrogen 1.87 g $N–NH_4 \cdot m^{-2} \cdot d^{-1}$. The study confirmed the usefulness of constructed wetland method application for separate treatment the reject waters from aerobic sewage sludge stabilization. At present, studies on the object designed for reject waters purification for a real scale, were begun. It is the first object of that type, installed in dairy sewage treatment plant in Poland, and it was designed as a result of the research work realized by the author in 2007–2009.

Keywords: reject water, constructed wetlands, biogenic, nutrients and organic substances

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Agro-food industry works, namely dairy plants, dominate in north-eastern Poland. There are nine such plants that are equipped with individual wastewater treatment systems in Podlasie region. In practice, all objects need to be modernized due to increasing sewage load resulting from arising production at these works. Increasing amounts of sewage sludge and reject water generated during their processing is a consequence. Reject water is characterized by significant content of ammonium nitrogen in relation to the raw wastewaters disposed from dairy plants to own wastewater treatment plant or just to a sewage system and municipal wastewater treatment plant. It is returned to the beginning of the purification process, which makes periodical disturbances in stable and efficient sewage treatment.

Separated treatment of reject water can be carried out by means of different methods. There are: precipitation, de-aeration using warm air stream, ammonia evaporation using steam, ionic exchange, as well as biological methods such as conventional and unconventional nitrogen removal: ANAMMOX process, BABE method, shortened nitrification and denitrification process, including SHARON method, combinations of ANAMMOX and shortened nitrification and denitrification process as, for instance, CANON & OLAND method [1, 2]. The SHARON method (*Single Reactor System for High-Rate Ammonia Removal Over Nitrite*) is a full-scale process for reject waters purification. It uses the dependence of the bacterial growth rate on temperature, thus ammonium compounds and nitrites oxidation rate on temperature, as well as differences between growth rates of nitrosobacteria and nitrobacteria [3, 4]. Applying expensive physicochemical method is reasonable in the case of large municipal sewage treatment plants that usually apply the anaerobic sludge stabilization. In the case of smaller objects that stabilize sewage sludge in aerobic way, including dairy plants, applying simpler and much cheaper methods of separate reject water purification, is more suitable.

Studies related to constructed wetlands began in 2006, when the first installation based on a *vertical constructed wetland* (VF-CW) was built within the largest dairy sewage treatment plant in north-eastern Poland (Mlekovita, Wysokie Mazowieckie). In 2007, another installation based on a vertical wetland was launched also within Mlekovita Ltd. (Bielsk Podlaski), while a hybrid system (consisting of vertical plus horizontal flow constructed wetland beds) was initiated in Wysokie Mazowickie can work in cycles, while horizontal ones work continuously. Their application ways are recognized and described in literature [5–7]. The constructed wetland systems are characterized by a simple operation and no chemicals applied. During their work, no wastes characteristic for active sediment method, are generated. However, needs of large area, difficulties in plant adaptation on mineral bed, and oscillations of the purification efficiency within a year, are their main shortcomings. A properly designed and built object can be successfully exploited for many years.

Advantages of the constructed wetland method led to its utilizing for household, municipal, industrial, agricultural, and gas station sewage, rainfall water, reject water from waste dumps, area runoff from cultivated fields and airfield purification. It is also applied to process the sewage sludge. Low energy-consumption, simple construction, and cheap exploitation are the main merits from using constructed wetlands for sewage sludge processing.

Table 1 presents list of general working parameters of two dairy wastewater treatment plants that were analyzed by the author in a view of constructed wetland system incorporation. It contains basic parameters such as amounts of sewage and reject water, equivalent for individual objects referring to raw sewage and reject water quantities. The amounts of ammonium nitrogen load in raw sewage and reject water were also determined.

Table 1

Basic characteristic of chosen dairy wastewater plants belonging to Mlekovita in 2009

Parameter	Unit	Bielsk Podlaski W.W.T.P.	Wysokie Mazowieckie W.W.T.P.
Sewage quantity	$[m^3 \cdot d^{-1}]$	570	5240
P.E. of sewage	—	8740	240000
Load of ammonia nitrogen in raw sewage	$[kg\ N\text{-}NH_4 \cdot d^{-1}]$	1.5	9.43
Reject water quantity	$[m^3 \cdot d^{-1}]$	25	530
P.E. of reject water	—	60	1060
Load of ammonia nitrogen in reject water	$[kg\ N\text{-}NH_4 \cdot d^{-1}]$	0.32	5.7

Due to a composition of reject water generated during aerobic sludge stabilization, the research installations were built on a base of vertical flow constructed wetland system that assures the nitrification process. It was observed that the quantity of reject water from aerobic sewage sludge stabilization in dairy wastewater treatment plant is periodically growing. The study was aimed at evaluating the usefulness of high loaded ($0.25\ m \cdot d^{-1}$) vertical flow constructed wetland to remove organic and biogenic compounds from reject water.

Material and methods

The paper present results from studies upon one of the installations designed by the author to perform research within the project *Evaluation of constructed wetland usefulness to purify reject water from aerobic sludge treatment in dairy wastewater treatment plants*. The system works in dairy sewage treatment plant in Bielsk Podlaski and consists of the retention tank, vertical flow bed, and measuring system. Reject water from aerobic sewage sludge processing are subject to purification. The sludge stabilization occurs simultaneously to dairy sewage purification process, which is a typical solution in Promlecz type systems designed for treatment the dairy sewage. Long time when the sewage is retained in an aeration chamber, ensures the sludge stabilization. The excessive sludge is disposed to a thickener, then to dehydration. Separated chambers to active sludge regeneration are used in a sludge course [6]. The vertical flow constructed wetland applied in the research, was designed according to recommendations by Brix [7], Cooper [8], and Obarska-Pempkowiak [9]. It is of 20 m^2 surface area and bed layer thickness of 0.65 m. It is grown by specially prepared seedlings of three-year-old *Phragmities australis.* Figure 1 illustrates the cross-section of the constructed wetland used in the study. It consists of three bed layers (gravel,

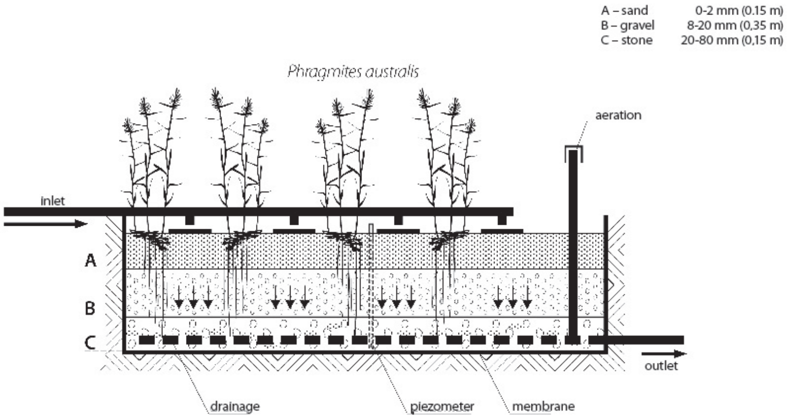

Fig. 1. Cross-section of vertical bed

sand, and stones), reject water is supplied by PVC piping (ID 50 mm), the drainage system is mounted at the bottom, and the ventilation system is also provided. The passive ventilation improves the bed aeration. During the studies made by the author in 2006–2007, the hydraulic load ranged within 0.05–0.15 m · d^{-1} [10, 11]. Due to a prepared project of incorporating the system into the real process, the installation abilities were also verified at higher unit load of bed surface (0.25 m · d^{-1}). Recirculation was not used during this experiment.

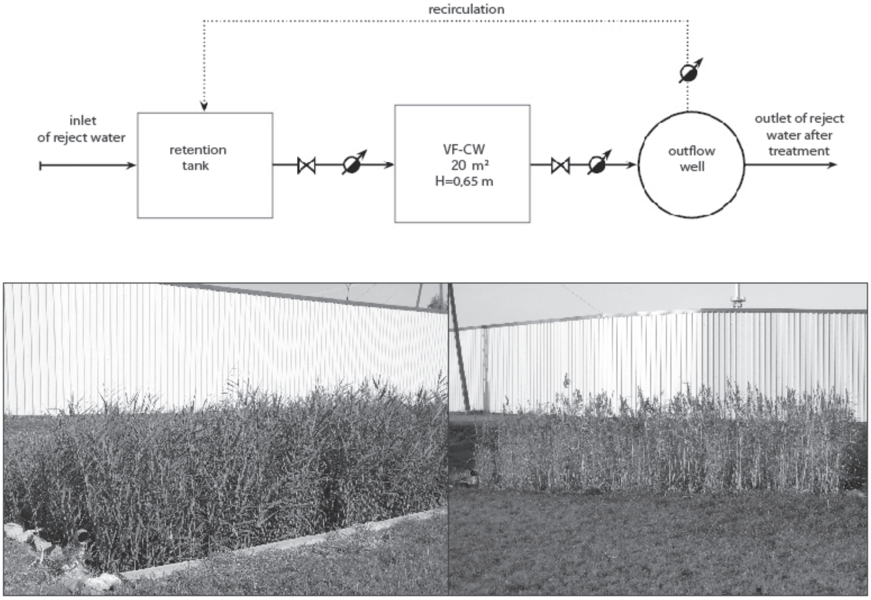

Fig. 2. Flow diagram of the research installation

Figure 2 presents the scheme of the research installation along with the photos taken in spring and autumn 2008. Studies were performed since August till October 2008, samples of reject water supplying the bed, as well as those from the outlet, were collected every 4 days, which made 12 measurement series in total.

The determinations included: BOD_5, COD, TOC, TKN, ammonium nitrogen, nitrates(V), total phosphorus, and suspensions. Table 2 containing study results, also presents permissible values for purified wastewaters disposed from dairy wastewater treatment plant in Bielsk Podlaski to a receiver [12].

Analyses were performed in laboratory of Department of Technology in Engineering and Environment Protection, Technical University in Bialystok. All determinations were performed in accordance to Polish Norms.

Results and discussion

Parameters of dairy sewage, sewage sludge and reject water presented in Tables 1 and 2 confirm that the removal of ammonium nitrogen should be focused on in the case of the separate reject water treatment. Its load in reject water in Bielsk Podlaski treatment plant reached 21.3 % in relation to that in raw dairy sewage. In the other presented object, that value achieved up to 62.4 %. Results from studies upon reject water treatment after statistical processing are presented in Table 2.

The BOD_5 value in reject waters supplied to the vertical flow constructed wetland amounted from 96 to 154 mg $O_2 \cdot dm^{-3}$. The mean value of BOD_5 in reject waters supplied to the purification was at the level of 118.6 mg $O_2 \cdot dm^{-3}$, which at hydraulic load of 0.25 $m \cdot d^{-1}$, resulted in load indicator of 29.6 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$. Average BOD_5 value at the outlet from the installation was 36.2 mg $O_2 \cdot dm^{-3}$, which made the decrease by 69.4 %. Considering COD, mean efficiency of the installation was 53.7 %, while TOC 62.5 %. The Kjeldahl's nitrogen removal efficiency amounted to 55.8 %, whereas ammonium nitrogen 72.1 %, on average. Analysis of the nitrogen forms contents in reject water before and after treatment indicated that the nitrification process occurred. Vertical flow constructed wetland supplied in a cyclic way works under aerobic conditions. The bed aeration is supported by a passive aeration system. The mean bed loading with ammonium nitrogen was 2.6 g $N–NH_4 \cdot m^{-2} \cdot d^{-1}$.

Efficiency of organic substance removal for vertical flow constructed wetland was 20.6 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$, while for ammonium nitrogen 1.87 g $N–NH_4 \cdot m^{-2} \cdot d^{-1}$, on average. According to author's earlier studies (carried out in 2007) involving the same installation, the efficiency of BOD_5 was 11.5 g $BOD_5 \cdot m^{-2} \cdot d^{-1}$. The increase of purification efficiency can be elucidated with the fact that here presented results were achieved in two years of the installation operating and studies were performed during the most intensive plant vegetation.

The average ammonium nitrogen removal efficiency for the other installation, where studies upon reject waters purification were also conducted, amounted from about 1.77 to 1.79 g $N–NH_4 \cdot m^{-2} \cdot d^{-1}$ in 2007, depending on the bed layer thickness [10, 13]. Phosphorus removal efficiency was poor amounting to 19.4 %, while average phosphorus content at the outlet from the experimental installation was 5.8 mg $P \cdot dm^{-3}$

Table 2

Effectiveness of constructed wetland in Mlekovita Bielsk Podlaski for reject water treatment

Parameter	BOD_5	COD	TOC	N-TKN	$N\text{-}NH_4$	$N\text{-}NO_3$	Total P
	$[mg\ O_2 \cdot dm^{-3}]$		$[mg\ C \cdot dm^{-3}]$	$[mg\ N \cdot dm^{-3}]$	$[mg\ N\text{-}NH_4 \cdot dm^{-3}]$	$[mg\ N\text{-}NO_3 \cdot dm^{-3}]$	$[mg\ P \cdot dm^{-3}]$
Inlet to VF-CW							
Minimum	96.0	196.0	32.0	15.3	8.2	0.4	8.1
Maximum	154.0	255.0	48.0	24.2	14.7	1.7	4.1
Mean	118.6	242.1	38.4	17.2	10.4	1.9	7.2
Standard deviation	11.2	16.3	4.2	2.1	1.1	0.2	0.5
Outlet from VF-CW							
Minimum	24.0	92.0	10.0	7.0	1.4	8.2	5.2
Maximum	39.0	119.0	16.0	9.1	3.6	10.1	6.1
Mean	36.2	112.0	14.4	7.6	2.9	9.7	5.8
Standard deviation	5.1	8.7	1.6	1.1	0.3	1.2	0.5
Limits for dairy wastewater after treatment in Mlekovita Bielsk Podlaski	50	125	30	30	10	—	1.5
Mean effectiveness of reject water treatment	69.4 %	53.7 %	62.5 %	55.8 %	72.1 %	—	19.4 %

at permissible value for dairy sewage treatment plant in Bielsk Podlaski of 1.5 mg $P \cdot dm^{-3}$. The constructed wetlands are not adapted to intensive phosphorus removal. In order to improve the removal efficiency, special filling in a form of lime gravel or separate filters for its removing should be applied [14]. Nitrate nitrogen content was 9.7 mg $N–NO_3 \cdot dm^{-3}$ after purification complete while 1.9 mg $N–NO_3 \cdot dm^{-3}$ before . In the case of Bielsk Podlaski dairy wastewater treatment plant, reject water after purification may be returned to the beginning of purification process or directly to the active sludge chamber that works under aerobic conditions. If a dairy sewage treatment plant operates using the chambers for intensive phosphorus removal by biological means, reject water, after separate pre-purifying, should be directed to the denitrification chamber in such a way not to disturb the process of phosphorus removal from the sewage.

Conclusions

1. The vertical flow constructed wetland may be used to decrease the reciprocal load due to reject waters from aerobic sewage sludge processing in a dairy wastewater treatment plant. Necessary surface area of the constructed wetland should be calculated on a base of the bed surface load both due to BOD_5 and ammonium nitrogen.

2. Vertical flow bed ensures a high effect of organic substance removal measured with such indicators as BOD, COD, or TOC. The effective nitrification is possible at a hydraulic load reaching to 0.25 $m \cdot d^{-1}$.

3. In dairy sewage treatment plants that do not use intensive removal of phosphorus by biological means, reject water – after purification – should be directed to the beginning of the sewage purification process. Due to a low efficiency of phosphorus removal in VF-CW system and requirements on purified sewage quality, it is necessary to apply additional elements for its removal or use special filling making possible to phosphorus removal.

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USUWANIE SUBSTANCJI ORGANICZNEJ ORAZ ZWIĄZKÓW BIOGENNYCH Z ODCIEKÓW METODĄ HYDROFITOWĄ

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Abstrakt: W województwie podlaskim działa 16 zakładów przetwórstwa mleczarskiego, z których 9 korzysta z indywidualnych systemów oczyszczania ścieków, pozostałe zaś odprowadzają ścieki do oczyszczalni komunalnych. Równoważna Liczba Mieszkańców (RLM) dla obiektów indywidualnych waha się od 7000 do niemal 240000, przy przepływie od 500 do 5500 m^3 ścieków na dobę. Większość obiektów pochodzi z lat 70. ubiegłego wieku. Są one przeciążone ładunkiem zanieczyszczeń ze względu na wzrost produkcji w zakładach obserwowany od ponad 20 lat. Wzrost ładunku ścieków spowodował zwiększenie ilości osadów ściekowych oraz odcieków z ich przeróbki. Odcieki są z reguły kierowane na początek procesu oczyszczania, stanowiąc znaczne obciążenie, szczególnie w odniesieniu do azotu amonowego. Jedną z możliwości zmniejszenia obciążenia oczyszczalni mleczarskiej jest zastosowanie wydzielonego oczyszczania odcieków z wykorzystaniem metody hydrofitowej. Metoda ta może stanowić alternatywę dla zaawansowanych i kosztownych technologii przeznaczonych do oczyszczania odcieków z oczyszczalni stosujących beztlenowa stabilizację osadów. Wykonane w okresie sierpień–październik 2008 r. badania przeprowadzono dla instalacji badawczej zaprojektowaną przez autora i działającą na terenie oczyszczalni ścieków mleczarskich w Bielsku Podlaskim. Oczyszczaniu poddano odcieki powstające w komorze zagęszczania osadu.

Wartości średnie wskaźników zanieczyszczeń w odciekach poddanych oczyszczaniu wynosiły: BZT_5 – 118,6 mg $O_2 \cdot dm^{-3}$, ChZT – 242,1 mg $O_2 \cdot dm^{-3}$, azot Kjeldahla – 17,2 mg $N_{TKN} \cdot dm^{-3}$, azot amonowy – 10,4 mg $N \cdot dm^{-3}$ oraz fosfor całkowity – 7,2 mg $P_T \cdot dm^{-3}$. Średnia efektywność usuwania wynosiła 69,4% BZT_5, 53,7% ChZT, 55,8% azotu Kjeldahla, 72,1% azotu amonowego i 19,4% fosforu całkowitego. Osiągnięto średni efekt usuwania substancji organicznej mierzonej przez BZT_5 na poziomie 20,6 $BZT_5 \cdot m^{-2} \cdot d^{-1}$, natomiast azotu amonowego 1,87 g $N\text{–}NH_4 \cdot m^{-2} \cdot d^{-1}$. Na podstawie uzyskanych wyników stwierdzono możliwość zastosowania metody hydrofitowej do wydzielonego oczyszczania odcieków z tlenowej przeróbki osadów ściekowych. Obecnie rozpoczęto badania na obiekcie zaprojektowanym do oczyszczania odcieków w skali rzeczywistej. Jest to pierwszy tego typu obiekt w oczyszczalni mleczarskiej na terenie Polski, który powstał jako wdrożenie wyniku pracy badawczej zrealizowanej przez autora w latach 2007–2009.

Słowa kluczowe: odcieki, złoża hydrofitowe, biogeny, związki organiczne

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ASSESSMENT OF HEAVY METALS CONTAMINATION IN RECREATIONAL PARKS OF POZNAN

OCENA STANU ZANIECZYSZCZENIA METALAMI CIĘŻKIMI W REKREACYJNYCH PARKACH POZNANIA (POLSKA)

Abstract: City Recreational Parks (RP) exert important functions for inhabitants of great agglomerations. They create peculiar ecosystem subjected to high pressure of anthropogenic factors (ie, motorization, maintenance, dusts), which may be a source of heavy metal contamination. Four parks located within the city Poznan have been: RP Marcinkowski (RPM), RP Solacki (RPS), RP Wodziczko (RPW) and RP Piatkowo (RPP). The aim of the work was to apply different quantitative methods for assessing heavy metal contamination state of these parks and to outline the encountered difficulties in the choice of the appropriate method.

On the basis of the assessment made by the IUNG suggestion [16], it appeared, that soils of all Recreational Parks may be considered as not contaminated by Pb, Cu and Zn. Cadmium was the main contaminant of RPM, RPS and RPW soils. The use of data representing the geochemical background [17], classifies soils of all parks as contaminated to polluted, even, whereas the evaluation made on the basis of mean heavy metal contents of Polish soils [18], stated that cadmium solely exceeded the reference value. Criteria reported in the Minister of Environment Directive [19] dealing with heavy metal thresholds seem to be less restrictive. The resulting assessment revealed that soils of investigated parks are free of any contamination.

Keywords: recreational parks, Poznan, soil, Pb, Cd, Cu, Zn, assessment methods, geochemical background

The development of city infrastructures along with transportation activities and heating systems generates a bulk of harmful by-products of which heavy metals are nowadays one of the most threatening pollutants. This is of great concern since heavy metals are not biodegradable in soils, so they tend to accumulate and persist in urban soils for a very long time [1, 2]. Lead, cadmium, nickel, copper and zinc are among others reported to cause the highest impact on living organisms, humans particularly [3, 4]. City dwellers, including a large number of children, most frequently spend their

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leisure time in green areas commonly termed as recreational parks, which are strictly under anthropogenic pressure (conservation, incorporation of composts before laying lawns, dry as well as wet dusts deposition). Assessment of the level of contamination or pollution has been made on the basis of several approaches dealing with the application of (phyto)biological methods [5, 6], chemical tests, whose data are confronted with broadly suggested and implemented guidelines (ie, background values, threshold values). The most frequently encountered difficulty relies in the choice of convincing and *site-adapted* guidelines [7–9], especially for city recreational parks.

The purpose of the study was to evaluate the level of heavy metals contamination of selected Poznan recreational parks by applying some implemented guidelines. The targeted approach is to outline the disparity and divergence in the elaboration of final decisions over the contamination or pollution state of a given environment.

Materials and methods

Short description of Recreational Parks (RP)

The investigated four *recreational parks* (RP) are located within the city-agglomeration Poznan and consist of: *Recreational Park Marcinkowski* (RPM, 52°24′15″N, 16°55′4″E), *Recreational Park Wodziczko* (RPW; 52°25′11″N, 16°54′56″E), *Recreational Park Solacki* (RPS; 52°25′17″N, 16°54′15″E) and *Recreational Park Piatkowo* (RPP; 52°27′27″N, 16°55′48″E). The RPM, formerly Frederic Schiller, was created during the period 1905–1906 and occupies currently an area of 9.4 hectares. It is located in the center of Poznan and surrounded by streets of heavy daily traffic. Trees and grasses form quite a similar area, which is yearly subjected to several maintenance activities. The Recreational Park Solacki (RPS) is one of the most beautiful leisure places and highly attended by Poznan dwellers. It was established within years 1907–1913 and actually its area spans to ca 14.63 hectares. The RPW occupies currently an area of 7.06 hectares. This park was decidedly set up in 1971–1972 and is laying close to the RPS. Recreational Park Piatkowo (RPP) was the widest investigated area consisting of ca 55.0 hectares. This complex (Park/Forest) was created in 1959 and involves a Reserve – Zurawiniec of 1.27 hectare. The site is located close to a housing estate Batory.

Soil sampling and chemical analyses

Soil samples were collected at two depths, 0–10 and 10–20 cm in October, 2009. This sampling procedure was adopted in order to outline the possible effect of conservation practices, lawn laying and other anthropogenic factors on metals levels. The amounts of samples are as follows: RPM – 36 samples, RPS – 52 samples, RPW – 32 samples and RPP – 34 samples.

Prior to chemical analyses, soils were air-dried and crushed to pass a 1.0 mm screen. Particle size composition was determined according to the aerometric method of Bouyoucos-Casagrande [10] and organic carbon ($C_{org.}$) by the Walkley-Black method as reported by Nelson and Sommers [11]. The pH was determined potentiometrically (*w/v*, 1:5) according to Polish Standard [12] in 0.010 mol $CaCl_2 \cdot dm^{-3}$. *Cation exchange capacity* (CEC) was obtained by the summation of exchangeable alkaline cations extracted by 1 mol $CH_3COONH_4 \cdot dm^{-3}$, pH 7.0 according to Thomas [13]. The *electrical conductivity* (EC) was determined conductometrically as described by Jackson [14]. Total contents of lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) were assayed by hot-digestion in *aqua regia* chemical test [15]. The quantitative-based assessment of heavy metals contamination (means of the layers 0–10 and 10–20 cm) was undertaken throughout:

– IUNG suggestion of soil contamination by heavy metals according to Kabata--Pendias et al [16],

– geochemical background values [17],

– mean heavy metal contents for Polish soils [18],

– Directive of the Minister of Environment for soil quality [19].

Computations were made by using the Excel® Sheet and simple statistical analysis by the Statgraphics Software facilities.

Results and discussion

Short overview

The last 15 years have been marked by significant trials and efforts aiming at implementing operational [16–18] and administrative [19] guidelines for the evaluation of heavy metal levels in Polish soils. The last ones concern in bulk, agricultural lands, forest environments, industrial areas, urban zones at large and specific ecosystems designated as protected zones. Most of the suggested guidelines were elaborated to be applied for broad soil characteristics and environmental conditions and are based on the total content of a given metal. Soil chemists and environmentalists frequently face the problem, which guideline(s) to use for a best estimation of the investigated site.

Data reported in Table 1 (mean of 0–10 and 10–20 cm) outline the specific characteristics of four recreational parks (RP) located within the city Poznan.

Table 1

Selected physical and chemical characteristics of soils within investigated Recreational Parks (RP) of the city Poznan (mean of 0–10 and 10–20 cm)

Parameter		RPM (n = 36)[a]	RPS (n = 52)[b]	RPW (n = 32)[c]	RPP (n = 34)[d]
Silt (0.002–0.05 mm)	$[g \cdot kg^{-1}]$	$397.2^{\alpha} \pm 139.3^{\beta}$	425.5 ± 143.2	227.5 ± 57.2	244.9 ± 129.9
Clay (< 0.002 mm)		136.8 ± 56.8	175.3 ± 79.6	111.9 ± 43.1	186.1 ± 59.0
$C_{org.}^{e}$		24.0 ± 5.5	25.0 ± 6.9	22.7 ± 4.1	17.5 ± 4.4
pH_{CaCl_2}		7.9 ± 0.13	7.2 ± 0.7	7.9 ± 0.07	6.8 ± 1.4
EC $[\mu S \cdot cm^{-1}]$		111.7 ± 28.2	125.9 ± 72.3	141.3 ± 72.9	67.2 ± 30.7
CEC $[mmol(+) \cdot kg^{-1}]$		107 ± 22.7	139 ± 79	125 ± 48	43 ± 31

[a, b, c, d] – Recreational Parks: Marcinkowski, Solacki, Wodziczko, Piatkowo, respectively; $^{\alpha}$ – Mean value ± $^{\beta}$ – Standard Deviation; [e] – $C_{org.} \cdot 1.724$ = *organic matter* (OM).

It should be mentioned the significantly low clay and silt content observed for the RPP (Recreational Park Piatkowo) site. The same was applied for the *cation exchange capacity* (CEC) amounting 43 mmol(+) · kg^{-1}. In the case of the three other parks, ie, RPM (Recreational Park Marcinkowski), RPS (Recreational Park Solacki) and RPW (Recreational Park Wodziczki), the reported physical and chemical properties appear to be at levels, which may efficiently control the geochemistry of heavy metals.

Quantitative-based assessment of heavy metals contamination

The IUNG suggestion [16]. A step to improve the interpretation of soil heavy metal contamination level was made in Poland, by distinguishing 6 contamination degrees, taking into account soil texture, organic matter content and *soil reaction* (pH). For the purpose of the current study, only the first degree, ie not contaminated (designated as natural content) was considered. Mean Cu, Zn, Pb and Cd contents are listed in Table 2 were used for assessing the contamination state of recreational parks.

Table 2

Total heavy metal content of soils within investigated Recreational Parks of the city Poznan (mean of 0–10 and 10–20 cm)

Metal	RPM (n = 36)[a]	RPS (n = 52)[b]	RPW (n = 32)[c]	RPP (n = 34)[d]
	[mg · kg^{-1}]			
Cu	$23.3^{\alpha} \pm 12.1^{\beta}$	19.4 ± 32.0	17.0 ± 10.2	10.5 ± 19.1
Zn	102.8 ± 47.4	58.6 ± 51.7	67.1 ± 63.6	41.8 ± 90.2
Pb	56.4 ± 25.0	32.0 ± 20.6	40.1 ± 18.2	13.0 ± 15.3
Cd	1.58 ± 0.42	2.12 ± 1.57	2.42 ± 1.58	0.87 ± 1.20

[a, b, c, d] – Recreational Parks: Marcinkowski, Solacki, Wodziczko, Piatkowo, respectively; $^{\alpha}$ – Mean value ± $^{\beta}$ – Standard Deviation.

Data reported in Table 3 revealed, that in any of the parks, the natural contents of Cu and Pb were not exceeded, except in the case of Zn, where its content in the RPM was higher *ca* 2.8 % as compared with the natural content.

Table 3

Heavy metal content used as "References" for the evaluation of contamination level of investigated Recreational Parks of the city Poznan

Metal	IUNG [16][1]	Czarnowska [17]	Kabata-Pendias and Pendias [18]	Minister of Environment Directive [19][2]
	[mg · kg^{-1}]			
Cu	40.0	7.1	10.4	150
Zn	100.0	30.0	41.7	300
Pb	70.0	9.8	14.2	100
Cd	1.0	0.18	0.29	4.0

[1] – 0^{o} contamination suggested as natural content for: share of particle fraction < 0.02 mm (range: 35–60 %), pH > 6.5, organic matter < 60 g · kg^{-1}, [2] – group B, soil sampling depth 0–0.3 m.

Most specifically is the contamination state related to Cd. It appears, that three (ie RPM, RPS, and RPW) of all parks exhibited a slightly high Cd contamination. The natural content (1.0 mg · kg^{-1}) was exceeded ca 38, 53 and 59 %, respectively, which implies, that additional care should be given to this metal. Practically, on the basis of the IUNG suggestion [16], the Recreational Park Piatkowo may be considered as not contaminated by all heavy metals.

The Geochemical background basis [17]. Strikingly interesting is the metal contamination state evaluated by applying the geochemical background as reported by Czarnowska [17]. On the basis of this evaluation it appeared, that all soils within the Recreational Parks were contaminated to even severely contaminated by investigated metals. Hence the reference geochemical background was exceeded for Cu from 48 to 228 %; Zn: 39–243 %; Pb: 33–476 % and Cd, incredibly from 383 to 1244 %! In other terms, it means from *ca* 1.5 to 3.3 times, 1.5 to 3.5 times, 1.3 to 5.8 times and 4.8 to 13.4 times, for Cu, Zn, Pb and Cd, respectively. Of all studied parks, it was found that the RPM was the most threatened by quite all metals, except Cd, whose levels were higher in RPS and RPW, confirming then the reported contamination state. Therefore, with respect to the current assessment, it may “roughly” be concluded, that investigated parks are not suitable for recreational purposes and should be disqualified, practically.

Mean heavy metal contents for Polish soils [18]. Data listed in Table 3 resume the content of heavy metals at surface soil layers for the whole Polish area, ie all ecosystems included. The levels of heavy metals as reported in Table 2 explicitly reveal, that of all investigated parks, only the Recreational Park Piatkowo (RPP) may be classified as not threatened by Cu, Zn, Pb, but by Cd, significantly, since the reference value was exceeded 3 times (in relative number 200 %). On the basis of metal contents, two parks ie RPS and RPW may be grouped in the same range of contamination state. The level of metals in these parks exceeded the reference values *ca* 1.8, 1.5, 2.5 and 15.7 times for Cu, Zn, Pb and Cd, respectively. This aspect may be partly explained by a relatively low content of metals in Polish soils, which implies that anthropogenic and mainly metallurgical site-specific contamination were not decisive in shaping mean heavy metal contents for Polish soils [18]. Furthermore, it may be mentioned that these values are much more close to geochemical backgrounds [17] as compared with metal contents according to IUNG suggestion [16].

Directive of the Minister of Environment for soil quality [19]. Criteria related to this Directive are formulated on the basis of permissible values of metals and chemicals according to functions or destiny of a given environment. Three groups have been set:

- A – protected lands on the basis of water legislative regulations and environmental protection,
- B – agricultural and forest lands, urban and inhabited zones,
- C – industrial, mining and communication areas.

Recreational Parks are classified in the group B and reference metal values used for contamination evaluation reported in Table 3. These limits seem to be exceptionally “less restrictive” as compared particularly to the IUNG suggestion [16] and mean heavy metal contents for Polish soils [18]. On this basis it may be observed, that investigated parks are all “free” of any threat related to these heavy metals! If we assume, that only 10 % of these references occur in readily active forms (ie water extractable) [20], therefore it should be expected the emergence of a potential concern related to specific contamination of attendees.

This is particularly probable for sandy soils, characterized most generally by low organic matter content. Such cases are often met under conditions of city recreational parks, for instance the Recreational Park Wodziczki (RPW) and Recreational Park Piatkowo (RPP). The applicability of the Directive of the Minister of Environment for soil quality [19] criteria for evaluating in-city contamination status must be supplemented by additional chemical soil tests in order to specify the fraction of the easily mobile (or labile) metals fractions.

Conclusions

1. On the basis of the IUNG suggestion [16], the soils of all Recreational Park may be considered as not contaminated by Pb, Cu and Zn. Cadmium was the main contaminant of RPM, RPS and RPW soils.
2. Contamination evaluation made on the basis of the Geochemical Background [17] revealed that all studied soils within the Recreational Parks were contaminated by all metals. Therefore, it may “roughly” be concluded, that investigated parks are not suitable for recreational purposes and should be disqualified, practically.
3. The levels of heavy metals in soils of investigated parks explicitly reveal, that only the Recreational Park Piatkowo (RPP) may be classified as not threatened by Cu, Zn, Pb, but by Cd, significantly, since the reference value (mean heavy metal contents for Polish soils [18]) was exceeded 3 times.
4. The Directive of the Minister of Environment for soil quality [19] seems to be “less restrictive” as compared particularly with the IUNG suggestion [16] and mean heavy metal contents for Polish soils [18]. On this basis it may be stated, that soils of investigated parks are all “free” of any threat related to these heavy metals.

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OCENA STANU ZANIECZYSZCZENIA METALAMI CIĘŻKIMI W REKREACYJNYCH PARKACH POZNANIA (POLSKA)

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Abstrakt: Rekreacyjne Parki (RP) miejskie spełniają ważne funkcje dla mieszkańców wielkich aglomeracji. Tworzą swoisty ekosystem, który jest poddany silnej presji czynników antropogenicznych (motoryzacja, prace pielęgnacyjne, pyły) mogących być źródłem zanieczyszczenia metali ciężkimi. Badaniami objęto cztery parki mieszczące się w mieście Poznań: RP Marcinkowskiego (RPM), RP Sołacki (RPS), RP Wodziczki (RPW) i RP Piątkowo (RPP). Celem pracy było zastosowanie różnych metod ilościowej oceny stanu zanieczyszczenia gleb tych parków metalami ciężkimi oraz wskazanie na trudności wyboru odpowiedniej metody.

Z oceny przeprowadzonej metodą zaproponowaną przez IUNG [16] wynika, że gleby wszystkich parków są niezanieczyszczone Cu, Zn i Pb. Kadm był głównym czynnikiem zanieczyszczającym gleby RPM, RPS i RPW. Gdy zastosowano jako kryterium tło geochemiczne [17], gleby parków zaliczono do grup od zanieczyszczonych do skażonych, natomiast według oceny dokonanej w oparciu o średnie zawartości metali ciężkich dla gleb polskich [18], tylko zawartość kadmu znacznie przekraczała wartość referencyjną. Kryteria zamieszczone w Rozporządzeniu Ministra Środowiska [19] odnośnie progowych zawartości metali ciężkich wydają się być „mniej restrykcyjne”. Ocena przeprowadzona w oparciu o te wartości progowe wykazała, że gleby badanych parków są wolne od zanieczyszczeń.

Słowa kluczowe: parki rekreacyjne, Poznań, gleba, Pb, Cd, Cu, Zn, metody oceny, tło geochemiczne

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CONCENTRATION OF HEAVY METALS IN COMPOST PRODUCED FROM MUNICIPAL SEWAGE SLUDGE FOR NATURAL REUSE

ZAWARTOŚĆ METALI CIĘŻKICH W KOMPOŚCIE Z KOMUNALNYCH OSADÓW ŚCIEKOWYCH WYKORZYSTYWANYM PRZYRODNICZO

Abstract: The studies aimed to evaluate the possibilities for agricultural management of sewage sludge from Municipal Sewage Treatment Plant in Sokolka. The content of macronutrients (N, P, K, Mg, Ca) and heavy metals (Cu, Cr, Cd, Ni, Pb, Hg) as well as disease-forming microorganisms (*Salmonella* rods, *Toxocara* spp., *Ascaris* sp.) were determined.

It was found out that the studied sludge was characterized with high fertilization value comparable with manure. Sludge included slight amounts of heavy metal ions, and they were very rich in nitrogen, phosphorus, calcium and magnesium. No disease-forming microorganisms were detected in the sludge. Sludge from Sewage Treatment Plant in Sokolka may be an alternative source of organic matter and some nutrients, as well as perfect substrate for soil humus formation.

Keywords: compost, heavy metals, sewage sludge

Sudden and continuous improvements in legal acts during few past years related to the environment protection favor the normalization of management of natural resources and their rational utilization. Different technologies of converting the sewage sludge into a product with changed properties are much more desirable. Converting the sludge into a compost or mineral-organic fertilizer gives the treatment plant much wider opportunities to dispose the sewage sludge. Disease-forming microorganisms are fought, their odors decrease or even disappear, and the consistence is improved due to the processes of sewage sludge neutralization. Not all types of sludge can be a component for fertilizers production. Directive on fertilizers and fertilizing [1] gives the possibility for sewage sludge to be considered as organic or organic-mineral fertilizers. However, it should be on mind, that a fertilizer made of sewage sludge has to meet the

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restrictions set in the decree announced by Ministry of Agriculture and Food Management, in which maintenance of particular contents of heavy metals, namely cadmium, mercury, arsenic, and lead, is one of the main criteria for the fertilizer to be incorporated to a circulation on a market. When sewage sludge is naturally managed, even that originated from small treatment plants, one should bear on mind: a valuable organic matter is returned to a nature and not that wastes are utilized at any price. In the case of uncertainty of chemical and biological composition, presence of excessive heavy metals levels, thus the probability of their incorporating into the natural environment, a continuous monitoring of the product quality should be carried out.

In most cases, dehydrated sewage sludge is a strenuous exploitation problem for any sewage treatment plant. The more so when dehydrated sludge cannot find a buyer, which is presented by data of GUS (*Central Statistical Office*) in the Table 1. Disposal of sewage sludge should be considered an integral part of the sewage treatment process. In connection with the significant progress in household sewage treatment, there arises the necessity to deal with the problem of disposal of the still growing amount of sewage. One of the known methods of sewage sludge disposal is composting [2, 3]. Composting is a biochemical process of decomposition of organic compounds present in municipal, industrial or sewage waste. Composting of sewage sludge is based on natural biochemical reactions, intensified in artificially created, optimal conditions, ensuring in addition the possibility of controlling those processes. As a result of this process, compost-organic fertilizer is obtained, whose smell and colour are similar to those of the forest bed, widely used in agriculture. The basic processes occurring during composting are: mineralization, humification, mouldering, rotting and carbonization.

Table 1

Sewage sludge produced in Poland and ways of its management [data of GUS]

Specification	2003	2004	2005	2006
	10^3 Mg dry mass per year			
Sewage sludge	446.5	476.1	486.1	501.3
Sewage sludge used in agriculture	58.4	66.9	66.0	80.6
Sewage sludge used for land reclamation	105.2	110.7	120.6	109.7
Sewage sludge applied to crops for the production of compost	19.7	29.7	27.4	28.1
Thermal sewage sludge disposal	6.3	1.4	6.2	4.5
Sewage sludge disposal by waste dump landfilling	164.9	162.7	150.7	147.1
Sewage sludge accumulated in the sewage treatment plant	751.8	751.8	782.7	790.9

The study aimed at evaluating the heavy metals contents in compost made of sewage sludge from municipal sewage treatment plant in Sokolka that can be used in agriculture depending on general macronutrients and heavy metals concentrations (Cu, Cr, Cd, Ni, Pb, Hg, Mg, Ca, N, P, K), as well as disease-forming microorganisms presence (*Salmonella* rods, *Toxocara* spp., *Ascaris* sp.).

Material and methods

The compost from Sokolka is made as a by-product in treatment plant Sokolka from municipal sewage sludge. Mechanical-biological treatment plant in Sokolka purifies household, municipal, and industrial sewage, namely dairy. The treatment plant is one of the few within Podlasie region, where the sludge management is comprehensively solved. The composting is carried out applying anaerobic-aerobic method. The sewage sludge dehydrated in filter-conveyor press is transported to another place, where it is mixed using automated devices with the carbon carrier – sawdust. At the beginning of the technology incorporation, the mixture was prepared by means of tractor and rotary tiller, which was very labor and time-consuming and large area were necessary. Moreover, two main components were inappropriately mixed together, which made the composting process was not accurate (Fig. 1).

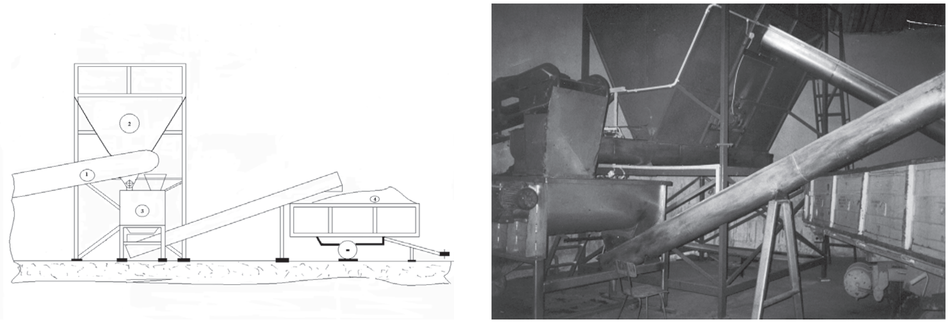

Fig. 1. Installation for sewage sludge and saw dust mixing

Such prepared mixture is transported then to an arched hall, where it is stocked in a pile and remained for 3 weeks, during which anaerobic processes associated with the temperature increase occur. After 3 weeks of anaerobic mixing, compost is formed in prisms (Fig. 2).

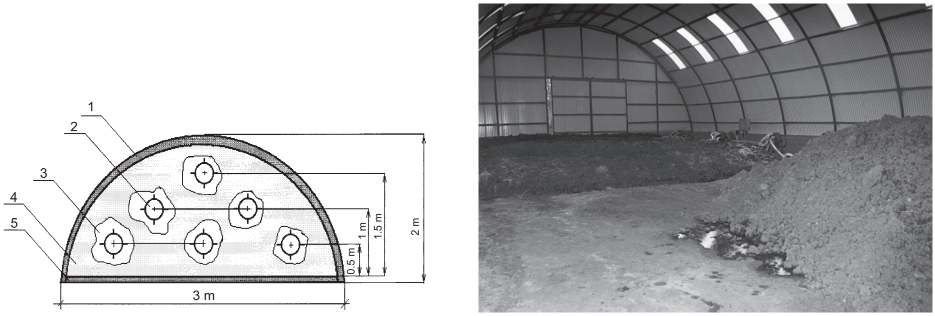

Fig. 2. Cross section of composting prism: 1 – cover layer (straw or paper board) – 30 cm; 2 – ventilation pipes; 3 – straw; 4 – compost mixture; 5 – prism floor

Grids are put into the prisms to make possible to release gases produced within the composting mixture out of the prism. Method of "sucking off" the gases increases the probability of atmospheric air penetration makes increased through all the prism section (Fig. 3).

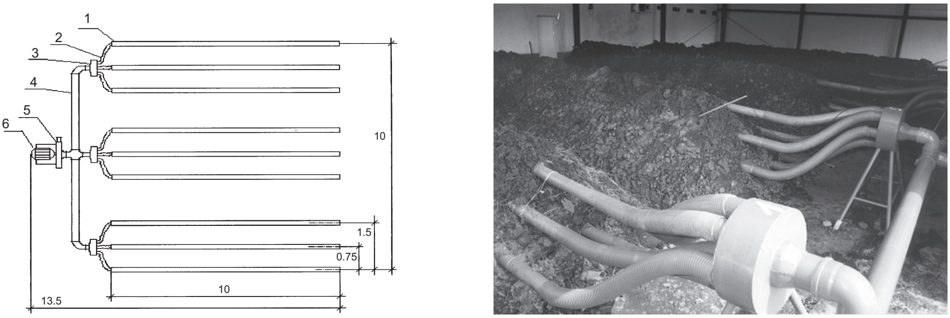

Fig. 3. Prism ventilation scheme: 1 – steel pipe with holes; 2 – spiro pipe; 3 – air separator; 4 – PVC pipes; 5 – high pressure ventilator; 6 – electric motor

Then ventilator is plugged into the grids. Its work ensures the aerobic conditions within the prism, but it should not cause the temperature drop below 40 ^{o}C. The aeration process persists about 14–20 days. After that period, the aerobic part of composting process is complete. Then, compost prisms are pulled down and compost is stored in arched hall for further processing. The compost maturation is the last stage of sewage sludge composting; it persists from three to six weeks depending on atmospheric conditions and its temperature. Low temperatures make the compost maturation should be prolonged.

In order to accelerate the compost maturation and to achieve the appropriate gravel-like structure, the compost should be poured several times using the device including tractor and manure spreader. Properly performed technology of sewage sludge composting process provides good organic fertilizer widely applicable in agriculture. Matured compost should have C:N ratio not greater than 20, and be characterized by brown color, garden ground flavor, and gravel-like or loose structure. Due to the fact that proper C:N ratio has to be reached in the final compost, dehydrated sewage sludge should be mixed with additional carbon source, eg wooden chips, straw, paper or sawdust. The amount of added carbon carrier should be precisely calculated to achieve C:N ratio equaled to 25–30. Considering Sokolka sewage sludge, the quantity of added sawdust is about 30 % of the compost weight. Total composting and seasoning duration of a single sewage sludge lot amounts to about 60–70 days. It is important to use straw for covering the grids, which enables a free gas flow out of the prism. Carbon content in the straw is similar to that in sawdust. For efficient composting process, following conditions should be maintained:

- temperature in a prism 40–50 ^{o}C (for minimum 3 weeks),
- humidity of composting mass 60–65 %,
- acidity of composting mass pH = 5.0–6.0.

The study was carried out using sewage sludge samples subject to composting process. Following heavy metals were determined in studied material: lead, copper, cadmium, nickel, zinc, and mercury. Mercury was determined by means of *atomic absorption spectrometry* coupled with *cold vapors technique* (CV-AAS), while other elements, applying *atomic emission spectrometry* with *inductively-coupled plasma* (ICP-AES). Fertilizing properties as well as microbiological and parasitological assays were performed in compost samples. Presence of disease-forming bacteria from *Salmonella* genus was identified by means of cultures on reproduction and differentiating-selecting mediums; results were verified due to biochemical determination using API20E tests. Live eggs of intestine parasites were isolated by shaking, washing out, centrifuging, and flotation, then microscopic observations. Total counts of mesophilic, spore, and thermophilic bacteria, as well as *Coli* and *Clostidium perfringens* titre were made according to Olanczuk-Neyman method [4].

Results and discussion

First of all, the agricultural utilization of sewage sludge is associated with its abundance in organic matter and nutrients. It makes real perspectives for improving the humus balance in Polish soils and fertilizing balance on the other hand. From economic and ecological points of view, hydration level of sludge, thus dry matter content, is an important parameter [5]. Studied compost contained from 34.2 to 60.5 % of dry matter (Table 2).

Table 2

The characteristic of compost

Specification	Properties						
Compost	Organic matter		Dry mass			Hydration	pH [-]
	[%]						
	67.5–67.86		34.2–60.5			39.5	6.15–6.7
	Manurial [% d.m.]						
	Ca	Mg	N_{og}	$N\text{-}NH_4^+$	$P_{P_2O_5}$	Na	K
	3.71–5.61	0.46–0.78	1.39–1.73	0.08–0.09	1.47–2.44	0.06–0.08	0.41–0.45
	Metal [mg · kg^{-1} d.m.]						
	Pb	Cu	Cd	Cr	Ni	Zn	Hg
	5.4–15.7	22.7–32.1	0.63–0.81	9.9–38.1	5.8–14.1	210–656	0.38–2.5
Permissible standard	500	800	10	500	100	2500	5

Not only organic nitrogen in sludge, but also its ammonium form that is directly available for plants, is important [6, 7]. Content of total nitrogen in Sokolka compost was 1.39–1.73 % in dry mass, while ammonium nitrogen available for plants 0.08–0.09 % of dry mass. Phosphorus is another biogenic element. Taking into account the phosphorus importance for plants and its circulation within the nature, the re-incorporation of the element contained in sewage sludge into the circulation for food production attracts more and more interests [7]. Examined compost was characterized by high phosphorus level ranging from 1.47 to 2.44 % in dry mass. Chemical analysis of sewage sludge revealed that it can also be counted to considerable source of calcium (3.71–5.61 % in dry mass) and magnesium (0.46–0.78 % of dry mass). Potassium is the most deficient component of sewage sludge, therefore additional potassium fertilization should be applied along with sewage sludge. It was found that most of studied sludge samples revealed great fertilization value, comparable with manure or even higher (Table 3).

Table 3

Total content of components in manure

Component	N	P	K	Ca	Mg	Organic matter
	[$g \cdot kg^{-1}$ of d.m.]					
Content	20	5.24	23.23	14.29	4.8	880.0

Examined compost contained significant quantities of nitrogen, phosphorus, calcium, magnesium, and organic substance (Table 2). Comparing to manure, the sewage sludge contained particularly large amounts of nitrogen and phosphorus: almost five times more phosphorus (compost 24.4; manure 5.24 $mg \cdot kg^{-1}$ d.m.), over eight times more nitrogen (compost 17.3; manure 2.0 $mg \cdot kg^{-1}$ d.m.), and four times more calcium (compost 56.1; manure 14.29 $mg \cdot kg^{-1}$ d.m.). Content of magnesium in compost (7.8 $mg \cdot kg^{-1}$ d.m.) was similar to that in manure (4.8 $mg \cdot kg^{-1}$ d.m.), whereas potassium content (4.5 $mg \cdot kg^{-1}$ d.m.) was even five times lower than that in manure (23.23 $mg \cdot kg^{-1}$ d.m.). Low potassium levels in sewage sludge results from very good solubility of potassium compounds [6]. Heavy metals ions contents in compost were many times lower than permissible values for agricultural utilization sludge [8, 9]. Such low content of heavy metals in sewage sludge reflects their low levels in sewage [10, 11]. The treatment plant in Sokolka purifies mainly municipal wastewaters with large percentage of dairy sewage. Chromium, zinc, lead, and nickel revealed the highest differentiations of their contents in studied sludge. Examined compost also showed great oscillations of mercury contents (0.30–2.5 $mg \cdot kg^{-1}$ d.m.), which could be the result of different qualities of sewage supplied by factories and works. Copper and cadmium contents remained at constant levels: 0.63–0.81 mg Cd $\cdot kg^{-1}$ d.m. and 22.7–32.1 mg Cu $\cdot kg^{-1}$ d.m..

No *Salmonella* rods nor parasitic eggs were found in analyzed compost (Table 4). Lack of parasite eggs, thus meeting the general sanitary requirements is an effect of composting process.

Studied sewage sludge meets sanitary requirements and those related to heavy metals contents, hence it can be used in agriculture. It may be an alternative source of organic matter and some nutrients, as well as a perfect substrate for soil humus forming [12–14]. Sludge abundant in organic matter, enriched in calcium and magnesium, may

Table 4

The results of microbiological and parasitological analysis of the sludge after composting process

Parameter	Result
Number of psychrophilic bacteria	$1.23 \cdot 10^7 \cdot g^{-1}$
Number of mesophilic bacteria	$1.04 \cdot 10^6 \cdot g^{-1}$
Number of bacterial spores	$3.0 \cdot 10^3 \cdot g^{-1}$
Number of termophilic bacteria	$1.5 \cdot 10^3 \cdot g^{-1}$
Coli titre	10^{-5}
Fecal *Coli* titre	0.0002
Clostridium perfringens titre	0.005
The present bacteria type of *Salmonella*	—
The present eggs of *Ascaris lumbricoides*	—
Number of funges	$7.21 \cdot 10^5 \cdot g^{-1}$

be very good mineral-organic fertilizer with de-acidifying properties, therefore it should be applied exclusively for agricultural purposes at rates calculated appropriately to a given soil composition [15].

Conclusions

Composting is a natural and controlled process of sewage sludge utilization, in which organic matter is decomposed under proper conditions of temperature, humidity and air access, and final product – compost – is the cheapest, the most easily available, and most appropriate for all crops, organic fertilizer. Compost, when continuously added into the soil, increases the humus content and improves the quality of poor soils under cultivation. Data referring to the quantities of produced sewage sludge and ways of its management (Table 1), it is obvious that at present, its natural utilization is the main direction of final sludge management in Poland. Performed analyses allowed for drawing following conclusions:

1. heavy metals contents in composted sewage sludge did not exceed limit values for its natural utilization,
2. compost is very abundant in biogenic elements – nitrogen and phosphorus – and it can be also considered as a significant source of calcium and magnesium,
3. disease-forming microorganisms were absent in studied sewage sludge, which is crucial for its sanitary qualifications,
4. compost made of Sokolka sewage sludge had great fertilization value and thus can be used in agriculture for fertilization purposes.

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ZAWARTOŚĆ METALI CIĘŻKICH W KOMPOŚCIE Z KOMUNALNYCH OSADÓW ŚCIEKOWYCH WYKORZYSTYWANYM PRZYRODNICZO

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Abstrakt: Celem pracy była ocena zawartości metali ciężkich w kompoście z komunalnych osadów ściekowych z Miejskiej Oczyszczalni Ścieków w Sokółce, wykorzystywanym przyrodniczo na podstawie zawartości w nich podstawowych makroelementów i metali ciężkich (Cu, Cr, Cd, Ni, Pb, Hg, Mg, Ca, N, P, K) oraz obecności mikroorganizmów chorobotwórczych (pałeczki *Salmonella* , *Toxocara* spp., *Ascaris* sp.).

Na podstawie przeprowadzonych analiz stwierdzono, że stężenia metali ciężkich w kompostowanym osadzie nie przekraczają wartości granicznych określonych przy przyrodniczym zagospodarowaniu osadów ściekowych. Kompost jest bardzo bogaty w pierwiastki biogenne – azot i fosfor i można go również traktować jako znaczące źródło wapnia i magnezu. W osadzie nie występowały mikroorganizmy chorobotwórcze, co jest bardzo ważne przy ich sanitarnym kwalifikowaniu. Kompost z Oczyszczalni ścieków w Sokółce ma dużą wartość nawozową i może być wykorzystywany w rolnictwie do celów nawozowych.

Słowa kluczowe: kompost, metale ciężkie, osad ściekowy

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INFLUENCE OF COMPOSTING SEWAGE SLUDGE ON CHANGE IN LEAD CONTENT IN SEQUENTIALLY SEPARATED FRACTIONS

WPŁYW KOMPOSTOWANIA OSADÓW ŚCIEKOWYCH NA ZMIANY ZAWARTOŚCI OŁOWIU WE FRAKCJACH WYDZIELONYCH SEKWENCYJNIE

Abstract: This article discusses lead quantitative changes occurring in sequentially separated fractions of sewage sludge composted together with straw and sawdust. The experiment was carried out in controlled conditions in four bioreactors. Experimental composts were prepared using sewage sludge obtained from a biological-chemical sewage treatment plant (composts 1 and 2) and sewage sludge derived from a mechanical-chemical sewage treatment plant (composts 3). Each compost mixture was characterized by the same proportion of sewage sludge (65 %), sawdust (30 %) and straw (5 %). Lead sequential extraction in experimental composts was performed using a modified BCR method.

The effect of composting of sludge derived from biological-chemical types of sewage treatment plants was 2.5–3.0 times lower lead content in water- and acid-soluble bonds (Fr. I). On the other hand, in the case of sludge obtained from the mechanical-chemical sewage treatment plant, the amount of lead in fraction I increased by 27 % in comparison with the content of this metal in samples collected at the initiation of the experiment. The composting process of the examined sewage sludge together with straw and sawdust exerted a similar impact on changes in the metal content in organic bonds (Fr. III) and residual fraction (Fr. IV). The quantities of lead found in fraction III of mature composts 1, 2 and 3 were, respectively, by 2.0, 1.5 and 4.0 times higher in comparison with the amounts of this element in experimental mixtures determined on the day of trial establishment. A reverse direction of quantitative changes was observed in the case of Pb determined in fraction IV of the experimental composts. Irrespective of the applied sewage sludge, content of the metal continued to increase up to the phase of cooling down and then, they declined during the phase of compost maturation. The above-described process was the strongest in conditions of compost 3. Share of lead in fraction I to IV reflected its quantitative changes expressed in absolute values. The experiments confirmed preferential development by Pb of poorly- and non-soluble bonds with the solid phase of composts.

Keywords: sewage sludge, compost, lead, sequential extraction

Despite the fact that sewage sludge composting is not a widely employed method of their management, nevertheless, its numerous advantages are well known [1, 2]. Among

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others, the fact is frequently stressed that it is a socially acceptable way of sewage sludge utilisation characterised, on the one hand, by costs lower than waste disposal and, on the other, less hazardous for the environment. Total metal content is commonly adopted to evaluate compost usefulness. However, these quantities do not reflect the real impact of metals on the environment because they do not describe mobility of metals [3–5]. In addition, as demonstrated by Ciba et al [6], elevated quantities of metals in composts need not necessarily mean that the utilisation of these materials as fertilisers will pose serious hazards to the soil. Therefore, according to numerous researchers [3, 7–9], it appears far more practical to determine the degree of bioavailability of metal contained in composts. This can be achieved, among others, using the method of sequential extraction which makes it possible to identify different bonds of metals with the solid phase of composts. It is very important issue because in sewage sludge composition and, consequently, also composts elements toxic for living organisms such as lead can be found.

During composting process, metals contained in sewage sludge can undergo various transformations changing their binding force. It is frequently emphasised that when composting sewage sludge, metal mobility and availability is reduced. It is assumed that metals which get into soils from composts are in chemically more stable bonds and are, therefore, less available for plants and are also less sensitive to leaching [10]. Other researcher [3, 11–13], however, maintain that elements increase their mobility in the course of biowaste composting.

In view of the above-mentioned controversies concerning the effect of composting on heavy metal mobility in composts, investigations were undertaken with the aim to determine quantitative lead changes in sequentially separated fractions that occurred during composting of three different sewage sludge with straw and sawdust.

Material and methods

The experiment was carried out in controlled conditions in four bioreactors. The bioreactor chambers of 125 dm^3 volume were isolated from external conditions. The schematic diagram of one chamber of the bioreactor together with its description can be found in a paper by Olszewski et al [14].

Experimental composts were prepared using sewage sludge obtained from a biological-chemical sewage treatment plant (sewage sludge 1 and 2 and respectively composts 1 and 2) and sewage sludge derived from a mechanical-chemical sewage treatment plant (sewage sludge 3 and respectively composts 3). Each compost mixture contained the same proportion of sewage sludge (65 %), sawdust (30 %) and straw (5 %). Selected properties of the components used in experiment are presented in an earlier paper [15]. Sewage sludge, straw and sawdust were well mixed prior to transferring to bioreactor chambers. The mixture was prepared so as to optimize the composting parameters ie, 60 % humidity and a C:N ratio of 6–10:1. The amount of air flowing throughout the composts corresponded to the volume of 4 $dm^3 \cdot min^{-1}$. Temperature was measured daily inside each compost. Four main phases were identified on the basis of the recorded temperatures. The characteristic of phases is presented in Table 1.

Table 1

Characteristic of composting phases

Phase	Length of time [days]	Range of temperature [°C]
(1) Mesophilic	1–2	40–45
(2) Thermophilic	13–18	70–80
(3) Cooling	8–14	45–30
(4) Mature compost	112–128	20–25

Each compost mixture was a separated object. Four subsamples of each compost were collected in the course of each phase. The gathered samples were mixed together. The material thus prepared was mean sample for each compost and phase.

Samples were dried out at 105 °C for a period 1 day. The dried samples was ground into a fine powder and stored in plastic bags at the temperature of 4 °C.

The total lead contents of sewage sludge, sawdust and wheat straw were determined by digestion with the *aqua regia* procedure ISO 1995 [16] and the obtained data are presented in Table 2.

Table 2

Total content of composted wastes [$mg \cdot kg^{-1}$]

Sewage sludge			Sawdust	Wheat straw
1	2	3		
30.20	33.24	38.96	1.78	0.80

The method of sequential extraction used in this study was developed by the *Community Bureau of References* – BCR (present Standards, Measurement and Testing Programme). The details of the experimental protocol are shown in Table 3.

Table 3

BCR sequential extraction procedure [17]

Fraction	Extracting agent	Extraction conditions	
		Time	Temperature
Fr I – Exchangeable, water and acid soluble	0.11 $mol \cdot dm^{-3}$ CH_3COOH (pH = 7.0)	16 h	20–25 °C
Fr II – Reducible, represents metals bound to iron and manganese oxides	0.5 $mol \cdot dm^{-3}$ NH_2OH-HCl (pH = 1.5)	16 h	20–25 °C
Fr III – Oxidisable, represents metals bound to organic matter and sulphides	30 % H_2O_2 (pH = 2.0) and next 1.0 $mol \cdot dm^{-3}$ CH_3COONH_4 (pH = 2.0)	1 h, 2 h, 16 h	20–25 °C, 85 °C, 20–25 °C
Fr IV – Residual, represents non-extractable metals bound with the strongest association to the crystalline structures of the minerals	*Aqua regia*	2.5 h	60–70 °C

Concentrations of lead in extracts and digests were determined by flame atomic absorption spectrometry (FAAS) using Varian Spectra AA 220 FS.

The analytical performance of the laboratory procedures was evaluated by analysis of BCR reference material CRM 145R (*trace elements in a sewage sludge*). Table 4 shows the data of three replicate analyses obtained for *aqua regia* extraction.

Table 4

Total lead content of reference material BCR 145R [mean ± standard deviation]

Found value [mg · kg^{-1}]	Certified value [mg · kg^{-1}]
234.5 ± 9.19	282.00 ± 11.28

Analyses of mean samples were carried out in three replicates. The obtained results were subjected to formal evaluation with the analysis of variance for double-factorial experiments using F test at the level of significance p = 0.95. Two basic experimental factors were taken into consideration in the course of the performed analysis: compost mixtures (A) and time of composting (B). The least significant differences were calculated using Tukey method at the level of significance of $\alpha = 0.05$ and then uniform groups within the factor level were established.

Results and discussion

A number of microbiological and chemical processes take place in the course of composting which result, among others, in the loss of organic matter causing, simultaneously quantitative changes in nutrients. According to Zorpas et al [18], the composting process can either dilute or concentrate quantities of metals which is the result of leaching from the decomposed organic matter or losses of the composted biomass. Literature on the subject provides data indicating decreases of the total lead content in mature composts [7, 19] as well as its increases [3, 20, 21]. In Authors own experiments, increases of the total metal contents were recorded in composts containing three different sewage sludge with additions of straw and sawdust, despite the fact that the effect of experimental factors was not confirmed statistically (Table 5).

Table 5

Influence of experimental factors on total lead content [mg · kg^{-1}]

Compost	Phase				Mean
	1	2	3	4	
1	20.18a	20.45a	25.31a	26.77a	*23.18a*
2	18.41a	18.48a	18.57a	21.33a	*19.20b*
3	16.56a	18.72a	18.95a	24.43a	*19.67b*

Total lead contents in mature composts were by 15 % (1) to 47 % (3) higher than at the beginning of composting process which should be attributed to the loss of organic matter (data not presented) and consequently higher lead amount. Irrespective of the applied experimental factors, total lead contents ranged from 16.56 to 26.77 mg · kg^{-1} (Table 5), hence, they did not exceed allowable threshold values specified in the regulation issued by the Minister of Agriculture and Rural Development [22]. Data from the literature on the subject provide information about lead quantities in composts similar to those from our investigations [8] as well as considerably higher [20].

Total metal content, although applied as a compulsory indicator of the degree of contamination of a given sample, fails to allow the assessment of metal mobility in the environment [3, 5, 19] and, therefore, it is essential to determine the form in which they occur. This statement acquires exceptional significance with reference to components applied directly into the soil as a source of organic matter and nutrients. According to Sidelko [9], the composting process involves changes in the form of metal binding which is the result of their complexing, precipitation and sorption. In this context, the above-mentioned researcher emphasises the importance of mineralisation which affects changes in the character of metal-organic complexes which determine metal mobility and availability. The composting process of sewage sludge together with various biowastes affects differences in the availability of chemical elements. Literature data provide information indicating both reduction [7, 23, 24] and increase in the mobility of chemical elements [3, 11, 12]. Lead sequential analysis carried out for composts 1 and 2 corroborated reduced solubility of this metal. Following the composting process, lead quantities in the water- and acid-soluble fractions in both composts were reduced by 60 to 70 % in comparison with those determined in the material at the beginning of the experiment (Table 6).

The same direction of quantitative changes of exchangeable lead was reported by other researchers [19, 24, 25]. On the other hand, a different direction of metal quantitative changes was recorded in conditions of compost 3 which developed on the basis of sewage sludge derived from a mechanical-biological sewage treatment plant. As evidenced by the data presented in Table 6, the Pb content in fraction I, beginning from the mesophilic phase until cooling, declined by 64 %. However, the maturation process of the mixture led to a significant (3.5 fold) increase in the level of the analysed metal in comparison with the one determined in the earlier phase (3.71 against 1.04 mg · kg^{-1}) (Table 6). Identical types of changes in Pb during composting were reported by He et al [19]. Moreover, higher quantities of exchangeable Pb in mature composts were also reported by Sidelko [9], Zheng et al [21] or Wong and Selvam [13]. In Authors own experiments, the determined Pb increase in fraction I of compost 3 could probably be attributed to a joint impact of the decomposing organic matter and increasing pH of the mixture (data not presented) which occurred during the composting process. According to Czekala [26], generally speaking, sewage sludge contains poor soluble organic compounds and the proportion of the organic carbon labile fraction is particularly low. However, it can be presumed that sewage sludge from the mechanical-chemical sewage treatment plant – in comparison with those obtained from the biological-chemical plant – contain a higher proportion of weak condensed, easily degradable humus compounds which, in the course of intensive degradation, could liberate certain quantities of lead.

Table 6

Influence of experimental factors on amount of lead in fractions of composts [mg · kg^{-1}]

Compost	Phase				Mean
	1	2	3	4	
Fraction I					
1	1.39a	1.12ab	0.54c	0.41cd	*0.87b*
2	1.08ab	1.49a	0.82bc	0.43cd	*0.95b*
3	2.91b	2.52b	1.04c	3.71a	*2.55a*
Fraction II					
1	3.91a	3.58a	3.04a	2.82a	*3.30b*
2	8.12a	7.28ab	5.92b	7.99a	*7.73a*
3	1.28ab	2.58a	2.28a	1.47a	*1.90c*
Fraction III					
1	7.21b	9.51b	13.56a	15.14a	*11.35a*
2	5.53b	6.02ab	6.36ab	8.84a	*6.69c*
3	4.04c	5.70bc	7.27b	16.13a	*8.28b*
Fraction IV					
1	6.65b	8.48ab	9.67a	6.53b	*7.84a*
2	6.31b	7.85ab	8.43a	6.96ab	*7.38ab*
3	5.92b	8.66a	10.13a	1.67c	*6.78b*
Sum of fraction					
1	19.17c	22.70b	26.83a	24.90ab	*23.40a*
2	21.04a	22.64a	21.54a	24.23a	*22.61a*
3	14.14c	19.46b	20.72ab	22.97a	*19.51b*

Sauve et al [27] maintain that pH increase favours elevated solubility of organic ligands which, in turn, easily forms complex with lead and, by doing so, increases its solubility and content. According to Czekala [11], changes associated with binding and releasing metals from numerous bonds with the compost solid phase should be attributed to their soluble organic matter. On average, for all the employed experimental factors, in the case of water- and acid-soluble fraction lead ranged from 0.41 to 3.71 mg · kg^{-1} and in the reduction fraction – from 1.28 to 8.12 mg · kg^{-1} (Table 6). Simultaneously, it should be emphases that, on average for all process phases, compost 3 contained by 3 times higher amount of Pb in fraction I (2.54 mg · kg^{-1}) and by 4 times lower in fraction II (1.90 mg · kg^{-1}) in comparison with composts 1 and 2 (Table 6).

Differences in the quantities of Pb between mixtures were reflected in shares of the metal in fraction I and II and in the sum of fraction (Fig. 1). However, these shares stressed the reduction of lead solubility more clearly. As evident from Fig. 1, irrespective of the applied sewage sludge, values of share of lead declined during composting process. This phenomenon became particularly conspicuous in the case of

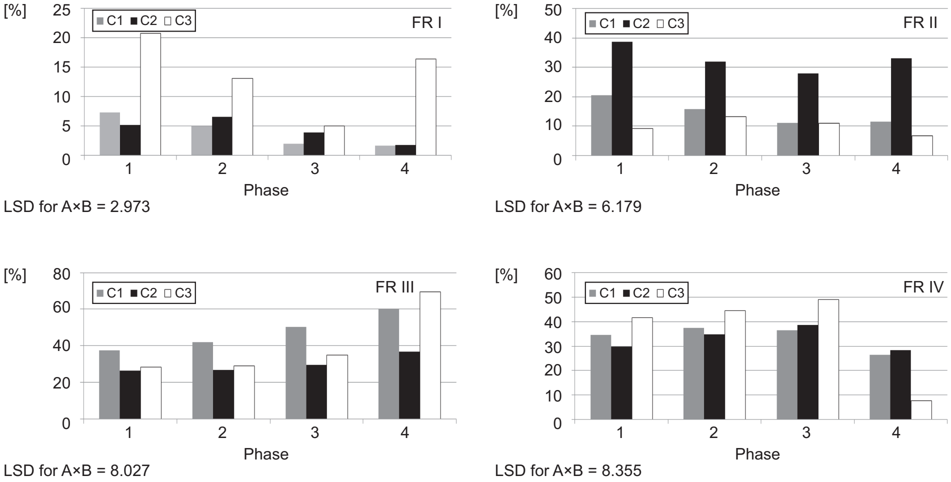

Fig. 1. Share of lead in fractions of composts [%] in dependence on experimental factors

composts 1 and 2 for which shares of the metal in fraction I were, respectively: 4 and 3 times higher on the day of experiment establishment than on its termination (Fig. 1).

Origins of the applied sewage sludge failed to cause differences in Pb quantities in the organic and residual fractions in a way so conspicuous as it was the case with regard to fractions I and II. As evident from the data in Table 6, Pb content in fractions III and IV ranged from 4.04 to 16.13 mg · kg^{-1} and from 1.67 to 10.13 mg · kg^{-1}, respectively. Irrespective of the examined compost, its maturation resulted in the increase of this metal in fraction III and its decline in fraction IV. The composting process of the examined mixtures up to the cooling phase favoured gradual increase of Pb quantities in the residual fraction. The content of the metal in these bonds was by 1.5 times higher in comparison with the content of this element determined in samples at the beginning of the trail. Maturation of the experimental composts 1, 2 and 3 reduced the content of lead in the residual fraction by, respectively: 32, 37 and 84 % (Table 6).

The strength of lead quantitative changes in fractions III and IV was the highest in compost 3. In comparison with the lead contents in samples collected during the mesophilic phase, the mature compost contained 4 times more metal in the organic fraction and 75 % less in the residual fraction (Table 6). In the case of the remaining mixtures, the composting process contributed to 1.5 to 2.0 times higher Pb amounts in fraction III.

Elevated quantities of the element in the organic fraction and its simultaneous decline in the residual fraction were also reported by Liu et al [12] who blamed it on the transformation of the residual lead into organic bonds. The above phenomenon should be interpreted on the basis of the transformations of the biowaste organic matter taking place during their composting. Chien et al [28] claim that, in the course of the process, quantities of organic compounds easily available to microorganisms are reduced at a simultaneous increase of fractions of organic compounds of aromatic structure which are characterised by high affinity for metal ions. In this context, the quality of sewage sludge becomes important. It is evident from the performed investigations that the organic matter of sludge derived from the mechanical-chemical sewage treatment plant was subject of more extensive transformations of this type and, therefore, stimulated more noticeably the transfer of lead from one kind of bonds to others.

Generally speaking, the literature on the subject emphasises reduction of the metal content in residual bonds [12, 13, 19, 25] which was also corroborated by Authors investigations. There is less agreement among researchers regarding the impact of composting on the quantitative Pb variability in fraction III representing compost organic bonds. Literature data, on the one hand, claim lack of such changes [19], their decline [12, 25] or their increase [21]. On top of that, such researchers as: Amir et al [7], Ozimek et al [8], Liu et al [12], He et al [19], Gondek [20], Zeng et al [24], He et al [25] emphasis quantitative domination of the discussed chemical element in poorly- and non-soluble bonds. The above-mentioned researchers estimate the share in this type of bonds at 54 to 75 % of its total amount. In the performed investigations, lead shares in fractions III and IV reflected its quantitative changes expressed in absolute values (Fig. 1). On average, for experimental factors, the values of shares ranged from 26.6 to 69.4 % for fraction III and from 7.6 to 49 % – for fraction IV (Fig. 1). Despite considerable differences between minimal and maximal values of shares, the performed experiments confirmed lead preferences for the development of poorly- and non-soluble bonds with the solid phase of composts.

Conclusions

1. The performed sequential analysis of compost samples representing consecutive stages of the composting process proved the fact that lead quantities in the separated fractions changed.
2. Composting of sewage sludge together with straw and sawdust resulted in reduced lead mobility.
3. The performed investigations confirmed the preference of lead to develop poorly- and non-soluble bonds with the solid phase of composts.

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WPŁYW KOMPOSTOWANIA OSADÓW ŚCIEKOWYCH NA ZMIANY ZAWARTOŚCI OŁOWIU WE FRAKCJACH WYDZIELONYCH SEKWENCYJNIE

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Abstrakt: Niniejsza praca prezentuje zmiany ilościowe ołowiu, jakie następowały w wydzielonych sekwencyjnie frakcjach osadów ściekowych kompostowanych ze słomą oraz trocinami. Doświadczenie prowadzono w warunkach kontrolowanych, w czterech bioreaktorach. Badane komposty przygotowano, wykorzystując 2 osady ściekowe pochodzące z biologiczno-chemicznych oczyszczalni ścieków (komposty 1 i 2) oraz osady z mechaniczno-chemicznej oczyszczalni ścieków (kompost 3). Każda mieszanka charakteryzowała się takim samym udziałem osadów (65 %), trocin (30 %) oraz słomy (5 %). Sekwencyjną ekstrakcję ołowiu w kompostach wykonano zmodyfikowaną metodą BCR.

Efektem kompostowania osadów z biologiczno-chemicznych typów oczyszczalni była 2,5–3,0-krotnie mniejsza zawartość ołowiu w połączeniach wodno- i kwasorozpuszczalnych (Fr. I). Natomiast kompostowanie osadów z mechaniczno-chemicznej oczyszczalni ścieków spowodowało wzrost zawartości ołowiu we frakcji I o 27 % w porównaniu z jego zawartością w próbkach reprezentujących fazę mezofilną. Proces kompostowania badanych osadów ściekowych ze słomą i trocinami wpłynął w podobny sposób na zmiany zawartości ołowiu w połączeniach organicznych (Fr. III) oraz rezydualnych (Fr. IV). Ilości metalu we frakcji III dojrzałych kompostów 1, 2 i 3 były większe odpowiednio o 2, 1,5 oraz 4,0 razy w stosunku do ilości pierwiastka w mieszankach pobranych w dniu założenia doświadczenia. Odwrotny kierunek zmian ilościowych stwierdzono w przypadku Pb oznaczonego we frakcji IV kompostów. Niezależnie od zastosowanych osadów ściekowych zawartości metalu wzrastały aż do fazy chłodzenia, po czym w fazie dojrzewania kompostów nastąpiło ich obniżenie. Proces ten najsilniej zaznaczył się w kompoście numer 3. Udziały ołowiu we frakcjach od I do IV odzwierciedlały jego zmiany ilościowe wyrażone w wartościach bezwzględnych. Badania potwierdziły preferencyjne tworzenie przez ołów trudno rozpuszczalnych i nierozpuszczalnych połączeń z fazą stałą kompostów.

Słowa kluczowe: osady ściekowe, kompost, ołów, ekstrakcja sekwencyjna

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HEAVY METAL CONTENTS AND THE SANITARY STATE AS AN ASSESSMENT OF RADISH (*Raphanus sativum* L.) QUALITY

ZAWARTOŚĆ METALI CIĘŻKICH I STAN SANITARNY JAKO OCENA JAKOŚCI RZODKIEWKI (*Raphanus sativum* L.)

Abstract: The research aimed at an assessment of health quality of radish originating from Krakow open air markets. The health quality was estimated on the basis of an analysis of the content and distribution of heavy metals in radish as well as its sanitary state. Heavy metal contents (Zn, Cu, Cd, Pb, Cr and Ni) were assessed in radish flesh, skin and leaves after dry mineralization and the ash dissolving in HNO_3 using ICP-EAS method. Microbiological analyses comprised determining *Coli* and *Salmonella* bacteria count as well as the number of anaerobic and spore forming bacteria (*Clostridium perfringens*).

Heavy metal contents in the studied radish fluctuated widely depending on the analyzed part. The highest contents of zinc, copper, chromium, lead and cadmium were assessed in leaves, lower in the skin and the lowest in radish flesh. Tested radish did not meet the consumer standards for zinc and cadmium. Presence of *Coli* bacteria was noted in 36 % of samples, *Salmonella* bacteria in 10 % and *Clostridium perfringens* only in 2 %.

Keywords: radish, heavy metals, sanitary state

Contamination of foods of plant origin poses a serious health problem. Lead and cadmium are counted among the main food pollutants which create the gravest hazard to human health, both because of their toxicological properties and common occurrence [1]. Zinc, copper, nickel, manganese and iron which in some pre-determined amounts are crucial for the proper course of physiological processes in living organisms, in excessive quantities may constitute a threat to human health [1–3]. Vegetables are valuable element of human diet providing a supplement of mineral salts and vitamins. Therefore, it is necessary to monitor vegetable quality focusing on the presence of

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potentially harmful substances [2, 3]. As has been stated by numerous authors, vegetable plants cultivated in soils and substrata polluted with heavy metals accumulate their excessive quantities which worsens the quality of the plants [4, 5]. Moreover, it has been demonstrated that in the regions under the influence of industrial emission and close to large city agglomerations heavy metal contents in both soil and plants raise considerably.

The research aimed at an assessment of health quality of radish originating from the open air markets in Krakow. Radish quality was assessed on the basis of the content and distribution of heavy metals and radish sanitary state.

Material and methods

The research was conducted at the turn of April and May 2008 on radish (*Raphanus sativus* L.). The studies covered 5 open air markets situated in Krakow. In most cases radish originated from horticultural and agricultural holdings located about 20–30 km from Krakow city agglomeration. 40 samples of radish were selected randomly for the tests. The purchased plant material was washed and divided into leaves, skin and flesh which were then dried at 80 ^{o}C in a drier with forced air flow. After drying the plant material was crushed and dry-mineralized. The ash was dissolved in HNO_3 acid in 1:2 ratio and in the obtained solution zinc, copper, nickel, chromium, lead and cadmium concentrations were assessed using *atomic emission spectrometry with inductively coupled argon plasma* (ISP-AES) on JY 238 ULTRACE apparatus (Jobin Von Emission). Microbiological tests were conducted to determine *Coli* count, *Salmonella* count and anaerobic spore forming bacteria (*Clostridium perfringens*) number [6–9]. For this purpose from each radish bunch stem and root nodosities were cut off from the leaves, weighed and placed in 100 cm^3 of sterile physiological salt solution. All was thoroughly shaken for 30 minutes. Microbiological analysis was conducted using serial dilution method. The subsequent dilutions were sown on a recommended microbiological medium and incubated. The grown colonies with features characteristic for a given group were counted after the adequate culturing time. The test was performed in three replications and the results were averaged and expressed in c.f.u. (*colony forming units*) per bunch and per 100 g of radish.

Obtained results were elaborated statistically using one-way ANOVA and Tukey test. The test was applied when no equality between the averages was revealed. The analysis of variance was conducted on significance level $\alpha = 0.05$. Arithmetic mean, *standard deviation* (SD), range and variability coefficient (V %) were determined. The results were elaborated by means of Statistic 8.0 programme.

Results and discussion

Heavy metal contents in plants depend in the first place on the plant species but also on the cultivar, development stage, plant part and heavy metal content in soil, and finally on numerous environmental factors. In the presented research the analysis of variance revealed that the content of assessed metals was significantly diversified for the analysed radish part regarding zinc, chromium, lead and cadmium (Table 1).

Table 1

The content of heavy metals in radish [mg · kg^{-1} d.m.]

Heavy metal	Part of radisch	Range	Mean	SD	V %[1]	$LSD_{0.05}$
Zn	Leaves	36.40–635.70	101.79^{b}	121.39	98	36.12
	Skin	43.20–360.25	81.17^{ab}	60.29	74	
	Flesh	14.88–252.98	48.95^{a}	50.20	96	
	Flesh + Skin	*35.11–300.07*	*77.30*[2]	*43.30*	*56*	
Cu	Leaves	2.30–58.30	5.84	9.93	84	ns[3]
	Skin	0–23.91	5.05	4.31	85	
	Flesh	1.20–4.13	2.26	0.80	36	
	Flesh + Skin	*2.39–28.20*	*4.38*	*3.45*	*79*	
Ni	Leaves	0–3.35	1.16	1.00	86	ns
	Skin	0–4.64	1.48	0.70	47	
	Flesh	0–6.04	1.04	0.55	53	
	Flesh + Skin	*0–4.67*	*0.80*	*0.56*	*70*	
Cr	Leaves	0.46–3.74	1.70^{c}	0.89	52	0.31
	Skin	0.24–2.89	0.60^{b}	0.51	86	
	Flesh	0–0.16	0.05^{a}	0.03	70	
	Flesh + Skin	*0.24–0.26*	*0.78*	*0.43*	*55*	
Pb	Leaves	0.29–12.40	2.18^{b}	2.13	98	0.64
	Skin	0.13–1.26	0.66^{b}	0.29	45	
	Flesh	0–0.56	0.07^{a}	0.12	69	
	Flesh + Skin	*0.31–0.52*	*0.97*	*0.74*	*76*	
Cd	Leaves	0.24–4.57	1.18^{b}	0.93	79	0.49
	Skin	0–0.46	0.78^{b}	1.35	45	
	Flesh	0.2–6.69	0.12^{a}	0.11	89	
	Flesh + Skin	*0.11–2.93*	*0.70*	*0.54*	*77*	

[1] Variability coefficient; [2] weighted arithmetic mean; [3] non significant.

Analysing the highest mean contents of metals, the tested radish parts may be ordered decreasingly starting from the highest content: leaves > skin > flesh. A significant relationship was demonstrated only for nickel: skin > leaves > flesh. The differences between the lowest and highest metal content in the leaves ranged from 8 (Cr) to 33-fold (Cu), in the skin from 1 (Pb) to 17-fold (Zn) and in the flesh from 1 (Cu) to 33-fold (Cd). A high divergence of the assessed metal contents in the analysed radish parts was corroborated by the calculated values of variability coefficients, which for Zn, Cu, Ni and Pb were the highest in the leaves, while for Cr and Cd in the flesh (Table 1).

Depending on the tested part, the range of heavy metal contents in radish fluctuated from 14.88 to 635.70 mg Zn; from 0 to 58.30 mg Cu; from 0 to 6.04 mg Ni; from 0 to 3.74 mg Cr; from 0 to 12.40 mg Pb and from 0 to 5.57 mg Cd $\cdot$ kg^{-1} d.m. (Table 1). In comparison with the skin, radish leaves contained on average one time higher amounts of zinc, copper and cadmium, almost three times higher of chromium and over three times bigger Pb quantities. On the other hand, in comparison with radish flesh over once bigger quantities of nickel, twice bigger of zinc and copper, 36-fold higher amounts of lead and almost 10-fold higher quantities of cadmium were assessed in radish leaves (Table 1).

Mobility of metals in radish was determined using translocation index (T_I). The parameter was calculated as a ratio of metal contents in leaves and skin to their contents in flesh (Fig. 1).

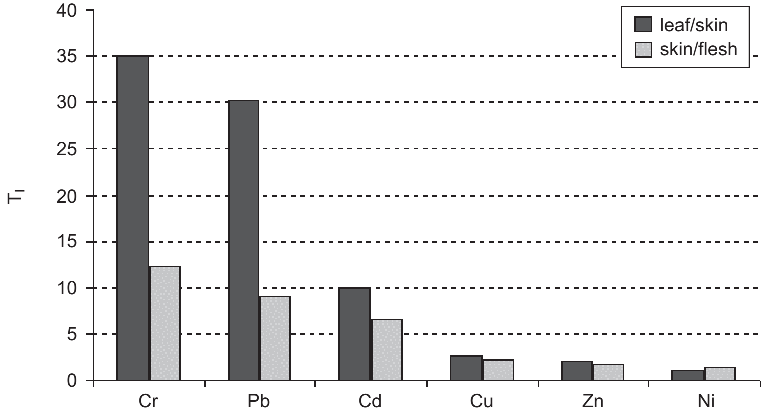

Fig. 1. Translocation coefficient of heavy metals in radish

The analysis of T_I value shows that radish nodosities (edible parts, flesh and skin) accumulated the greatest amounts of nickel, zinc and copper, slightly less cadmium and the least quantities of lead and chromium.

An interesting supplement to the above given data may be correlation coefficients computed between the contents of individual metals in radish depending on its analysed part (Table 2). As can be seen the highest number of correlations between the analysed metals was revealed in radish flesh. A significantly positive correlation was noted in flesh for Zn and Cr, Pb and Cd and subsequently for Cu and Cr and Pb, and also between Cr and Pb and for Cu and Cd. Investigations on the correlations between the contents of the analysed elements in radish skin showed a positive relationship for Zn and Ni and for Cr and Ni (Table 2). In leaves a significantly positive correlation was revealed for Cd and Zn and for Cr and Pb contents (Table 2). It should be noticed that in all three analysed plant parts a significantly positive correlation was noted between Pb and Cr, however it was the strongest in the flesh $r = 0.78$ ($p \le 0.001$), weaker in the skin $r = 0.52$ ($p \le 0.01$) and the weakest in the leaves $r = 0.37$ ($p \le 0.05$).

Table 2

Values of simple correlation coefficients between the content of heavy metals in the analyzed part of the radish

Heavy metal	Zn	Cu	Cr	Ni	Pb
Leaves					
Cu	–0.06				
Cr	–0.33	0.02			
Ni	0.13	0.04	0.26		
Pb	–0.10	–0.03	0.37*	0.30	
Cd	0.40*	–0.07	–0.14	0.66***	0.06
Flesh					
Cu	0.21				
Cr	0.62***	0.41*			
Ni	0.62***	–0.13	0.15		
Pb	0.55**	0.5**	0.78***	–0.01	
Cd	0.44*	0.07	0.14	0.61***	0.11
Skin					
Cu					
Cr	–0.20	0.06			
Ni	0.73**	–0.10	–0.09		
Pb	0.36	0.16	0.52**	0.44*	
Cd	0.15	–0.04	–0.05	0.16	0.06

Significant at: *** $p \le 0.001$, ** $p \le 0.01$, * $p \le 0.05$.

The assessment of the sanitary state of radish was presented in Table 3.

Table 3

Sanitary condition of radish

Parameter	*Coli* count		*Salmonella*		*Clostridium perfringens*	
	[cfu · bunch^{-1}]	[cfu · 100 g^{-1}]	[cfu · bunch^{-1}]	[cfu · 100 g^{-1}]	[cfu · bunch^{-1}]	[cfu · 100 g^{-1}]
Mean	135	80	6	3	1	1
Range	20–1300	11–664	20–120	17–61	10–20	6–10
% instances	36		10		2	

Presence of *Coli* and *Clostridium perfringens* bacteria evidences faecal contamination of not long ago. Presented research demonstrated that 64 % of radish samples (edible part flesh and skin) were clean of *Coli* bacteria, whereas 36 % were contaminated. On the other hand, spore forming bacteria *Clostridium perfringens* were found only in 2 % of samples and *Salmonella* in 10 % of samples (Table 3). The data demonstrate a good sanitary and hygienic state of the analysed radish purchased on the open air markets in Krakow.

A considerable percent of vegetables consumed by city dwellers originates from allotment gardens and plantations located in the suburban agricultural and horticultural holdings [10, 11]. It should be emphasized that vegetables belong to plants which very easily accumulate in their tissues excessive quantities of heavy metals, which change their chemical composition [4, 12]. Therefore, when cultivated in the regions subjected to city and industrial pollution they may not meet the quality criteria with respect to individual metals. Moreover, as reported by Filipek-Mazur et al [13] heavy metals, particularly high concentrations of lead and cadmium in plants for consumption, cause worsening of their quality and value as food. Norms of heavy metal contents in plants as suggested by Kabata-Pendias et al [14] admit consumption of plants with the following contents of heavy metals: ≤ 50 mg Zn; ≤ 20 mg Cu; ≤ 10 mg Ni; ≤ 1 mg Pb and ≤ 0.15 mg Cd · kg^{-1} d.m. Radish (edible part flesh and skin) assessment according to these norms shows that almost 40 % of the samples did not meet quality requirements of their usability for consumption due to excessive zinc concentrations whereas 65 % of samples because of cadmium content. Moreover, lead and cadmium contents in radish (edible part + skin) were assessed on the basis of European Commission Decree No. 1881/2006 of 19 December 2000 stating the highest admissible levels of some pollutants in foodstuffs [15]. According to the above-mentioned decree, the admissible content of lead and cadmium in root and stem vegetables should not exceed 0.1 mg Pb and 0.1 mg Cd · kg^{-1} f.m. Assuming a 10 % water content in the nodosities it corresponds to 1.0 mg Pb and Cd · kg^{-1} d.m. The studies demonstrated that none of the analysed radish samples exceeded the admissible lead level, whereas almost 10 % of radish samples revealed exceeded admissible cadmium level.

In conversion to 1 kg of fresh mass the studied radish contained in its nodosities (edible parts, flesh and skin) on average 7.73 mg Zn, 0.44 mg Cu, 0.08 mg Ni and Cr, 0.1 mg Pb and 0.07 mg Cd · kg^{-1} f.m. In the research conducted by Grembecka et al [3] radish originating from retail shops in the Gdansk region revealed almost thrice lower chromium content (0.03 mg · kg^{-1} f.m.) and 8-fold lower nickel content (0.01 mg · kg^{-1} f.m.) in comparison with radish bought on Krakow open air markets. The research of Tyksinski and Kurdubska [4] on cadmium and lead accumulation by radish indicated that increased doses of these metals in the substratum correspond to their elevated concentrations in radish nodosities. Moreover, the same authors revealed higher accumulation of cadmium and lead in plants cultivated in autumn than in spring. Average content of cadmium and lead in radish nodosities in autumn cultivation ranged from 0.96 to 11.57 mg Cd and from 4.49 to 20.83 mg Pb · kg^{-1} d.m., while in the spring cultivation metal concentrations were as follows: from 1.21 to 18.09 mg Cd and from 5.41 to 18.79 mg Pb · kg^{-1} d.m. [4]. High ability of radish to accumulate heavy metals is also testified by the fact that the above-mentioned authors registered high contents of cadmium and lead in radish cultivated in control combinations containing natural amounts of the metals. Jasiewicz [12] found that radish grown in soil containing 1.02 mg Cd · kg^{-1} d.m. accumulates in its nodosities 2.0 mg Cd · kg^{-1} d.m. Jurkowska et al [16] obtained similar results. The authors revealed that oil radish, spinach and fodder beet grown in the soil with natural cadmium and lead contents accumulated in their edible parts amounts of Cd and Pb which made them unsuitable for consumption [16].

The above quoted literature indicates that even at natural metal contents in the substratum, the admissible metal concentrations in vegetables are exceeded. It testifies a considerable ability of vegetables to accumulate heavy metals. The fact was confirmed by the results obtained by Curylo and Jasiewicz [17] who conducted research on carrot and celery and by Gaweda [18] in her studies on lettuce and radish.

Urbanized areas cover the city centre zones but also the peripheral parts of the cities. Increased content of heavy metals in soils is one of the pollution indicators in these areas [19]. Moreover, higher plants cultivated in the regions subjected to urban and industrial pollution may accumulate heavy metals even to the level hazardous to human health without showing any symptoms of toxicity [20–22]. According to the research of Rogoz and Opozda-Zuchmanska [21] zinc concentrations were exceeded in vegetables cultivated in the Krakow area and in the north-western regions, ie near Olkusz, Wadowice, Tyniec and Krzeszowice. Elevated cadmium concentrations in plants and soils in the north-western and north-eastern parts of Krakow in effect of dust emission from various industries were registered also by Gorlach and Gambus [23].

In conclusion excessive amounts of heavy metals and microbiological contamination occurring in foods of plant origin may cause various diseases. The sources of heavy metals may be both natural and anthropogenic. In Poland the arrangement of natural and anthropogenic factors may sometimes favour the uptake of greater metal amounts and their accumulation in usable plant parts [2, 24]. Moreover, as reported by numerous authors, plants growing in the regions under the influence of large industrial plants reveal higher contents of heavy metals than in agricultural areas [25].

Conclusions

1. The metals contents in radish ranged, depending on the analyzed part, from 14.88 to 635.70 mg Zn; from 0 to 58.30 mg Cu; from 0 to 6.04 mg Ni; from 0 to 3.74 mg Cr, from 0 to 12.40 mg Pb and from 0 to 5.57 mg Cd $\cdot$ kg^{-1} d.m.
2. The highest concentrations of zinc, copper, chromium, lead and cadmium were registered in leaves, lower in the skin and the lowest in radish flesh.
3. Radish did not fulfil consumption norms for zinc (40 % of analyzed samples) and cadmium (65 % of analyzed samples).
4. The sanitary state assessment of radish revealed *Coli* bacteria in 36 % of samples, *Salmonella* in 10 % of samples and *Clostridium perfringens* in 2 % of samples.

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ZAWARTOŚĆ METALI CIĘŻKICH I STAN SANITARNY JAKO OCENA JAKOŚCI RZODKIEWKI (*Raphanus sativum* L.)

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Abstrakt: Celem badań była ocena jakości zdrowotnej rzodkiewki pochodzącej z placów targowych Krakowa. Jakość zdrowotną oceniono na podstawie analizy zawartości i rozmieszczenia metali ciężkich w rzodkiewce, jak i jej stanu sanitarnego. Zawartość metali ciężkich (Zn, Cu, Cd, Pb, Cr, Ni) w miąższu, skórce i liściach rzodkiewki oznaczono metodą ICP-EAS po suchej mineralizacji i roztworzeniu popiołu w HNO_3. Analizy mikrobiologiczne obejmowały oznaczenie liczebność: bakterii z grupy coli, bakterii z rodzaju *Salmonella* oraz beztlenowych bakterii przetrwalnikujących *Clostridium perfringens*.

Zawartość metali ciężkich w badanej rzodkiewce wahała się w szerokim zakresie w zależności od analizowanej części. Największą zawartość cynku, miedzi, chromu, ołowiu i kadmu stwierdzono w liściach, mniejszą w skórce, a najmniejszą w miąższu rzodkiewki. Badana rzodkiewka nie spełniała norm konsumpcyjnych pod względem zawartości cynku i kadmu. Obecności bakterii grupy coli stwierdzono w 36 % próbkach, bakterii rodzaju *Salmonella* w 10 %, a *Clostridium perfringens* tylko w 2 %.

Słowa kluczowe: metale ciężkie, stan sanitarny, rzodkiewka

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TOTAL CONTENT OF MERCURY IN THE SOILS OF THE SURROUNDINGS OF LAFARGE-CEMENT PLANT IN MALOGOSZCZ

CAŁKOWITA ZAWARTOŚĆ RTĘCI W GLEBACH W OTOCZENIU ZAKŁADÓW CEMENTOWYCH „LAFARGE” W MAŁOGOSZCZY

Abstract: The aim of this research was to determine the total content of mercury in soils in the surroundings of “Lafarge” – Cement Plant in Malogoszcz. “Lafarge” factory is the source of emission of alkaline dusts. Soil samples were taken from six sites located in the various distances from the “Lafarge” factory. The content of mercury in soils was analyzed using AMA 254 spectrometer.

Investigated soils are classified as light soils with medium content of organic matter. The results of studies showed that soil samples in the vicinity of the source of dust emission had high pH and higher content of $CaCO_3$. It is caused by the continuous emission of alkaline dust from the factory. The content of mercury in tested soil samples was below the natural average content of mercury in mineral soils in Poland. Emission of cement dust from the “Lafarge” – Cement Plant does not influence the content of mercury in the investigated soils.

Keywords: cement dust, soils, mercury, alkalisation

Malogoszcz cement plant is a part of “Lafarge” Cement Company and is located in Malogoszcz, 35 km south-west from Kielce. Geographically this area is classified as Malopolska Upland [1]. This area is built from Jurassic limestone and Cretaceous sandstones. The cement plant started production in 1974 on the basis of its own natural resources – limestone and Jurassic marls from the quarry located 1 km from the factory. The factory produces clinker using dry method and there are four cement production lines. Cement manufacture requires very high temperatures, above 1400 ^{o}C and as a fuel different waste materials, often rich in heavy metals, are used for combustion [2, 3]. During the cement production a significant emission of gases and dusts occurs. Gases and dusts are captured by electrostatic precipitators and their effectiveness decide on pollution of the environment even excessive alkalization of surrounding soils and they

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are often the source of heavy metals even at the distance over 15 km [4]. Dusts emitted by a cement industry contain metals, including mercury. The mercury content in raw materials used for cement production as well as in fuels of different origin and composition, may significantly affect its concentration in the flue gases and the quantity of emission of this metal [4]. Mercury has the highest ability to release in the environment. It has high mobility due to the easy transition into various chemical forms, especially in the volatile form (Hg^0). Moreover, it is an element with one of the highest accumulation factor and the most toxic for living organisms [5]. High toxicity of mercury decided to treat it as a problem of global importance [6, 7].

The aim of the present study was to determine the level of total content of mercury in soils in the surroundings of "Lafarge" – Cement Plant in Malogoszcz.

Material and methods

The study has been done on soils sampled from the fields (arable soils) located in various distances from the "Lafarge" – Cement Plant in Malogoszcz (Table 1).

Table 1

Localizationof the research sites

Sampling site	Layer [cm]	Coordinates	Distance from the cement plant [m]
Zakrucze I	0–20	50°49′48.31″ N 20°17′01.53″ E	800
Zakrucze I	20–40		
Zakrucze II	0–20	50°49′53.99″ N 20°17′00.53″ E	850
Zakrucze II	20–40		
Lesnica I	0–20	50°49′54.12″ N 20°15′17.13″ E	700
Lesnica I	20–40		
Lesnica II	0–20	50°50′15.50″ N 20°14′31.35″ E	1700
Lesnica II	20–40		
Lesnica III	0–20	50°48′57.69″ N 20°15′09.14″ E	2900
Lesnica III	20–40		
Malogoszcz	0–20	50°48′57.69″ N 20°17′09.06″ E	2200
Malogoszcz	20–40		

Soil samples were taken from six sites, from two layers (surface) (0–20 cm) and (subsurface) (20–40 cm). In the dried and sieved material (∅ below 2 mm) the following soil properties were determined: pH in H_2O and in 1 mol · dm^{-3} KCl solution potentiometrically, the content of $CaCO_3$ – with the volumetric method by Scheibler, C-organic – according to Tiurin method. Texture was determined with the Casagrande areometric method, modified by Proszynski. Interpretation of the texture results was performed according to PTG (2008) classification [8]. The total content of mercury was determined in solid samples by atomic spectrometry method using AMA 254 mercury analyser [9]. Analyses were performed in three replications. The reliability of the results of the total Hg content was confirmed on the basis of certified reference material

TILL-3 and S-VM analysis. The results of Hg content are the arithmetical mean of three replicates with a standard deviation below 5 %.

Results and discussion

The analysis of granulation of soil samples taken from soils adjacent to "Lafarge" – Cement Plant indicates that their texture is corresponding to a granulometric group of loamy sand, sand, loam and sandy loam (Table 2). In terms of agricultural criteria they are qualified to light soils with the content of sand fraction in the range of 78–84 %, silt fraction 11–17 % and colloidal clay (∅ < 0.002 mm) 4–8 % [8]. Texture of the investigated soils indicates that they exhibit low buffer properties and are very vulnerable to pollution [10], however calcium carbonate from cement dust might affect these properties.

Table 2

Physicochemical properties of studied soils

Sample	Layer [cm]	Percentage of fraction with diameter [mm]			C-organic [$g \cdot kg^{-1}$]	$CaCO_3$ [%]	pH	
		2–0.05	0.05–0.002	< 0.002			H_2O	KCl
Zakrucze I	0–20	83	12	5	11.0	1.05	8.31	7.73
	20–40	78	14	8	10.8	0.38	8.07	7.53
Zakrucze II	0–20	84	11	5	8.3	1.26	7.84	7.61
	20–40	91	6	3	10.3	0.8	7.90	7.87
Lesnica I	0–20	81	13	6	16.3	0.42	7.93	7.42
	20–40	86	11	3	10.3	0.38	7.95	7.14
Lesnica II	0–20	82	14	4	18.4	0.42	6.40	5.82
	20–40	82	12	6	12.8	0.38	5.61	4.40
Lesnica III	0–20	79	15	6	12.0	0.42	5.66	4.84
	20–40	79	17	4	18.9	0.38	6.40	5.62
Malogoszcz	0–20	72	24	4	24.2	0.84	7.57	7.09
	20–40	63	29	8	20.3	0.84	7.75	7.15

The pH of investigated soils varied from acidic to alkaline. Soil pH was in the range of 5.61–8.31 (pH_{H_2O}) and exchangeable acidity pH_{KCl} was in the range of 4.40–7.87 (Table 2). In the investigated samples predominate soils with neutral and alkaline pH, which should be attributed to a long-term impact of cement dust emission, which caused the alkalization of soils [11]. The highest values of pH have soil samples taken from the closest neighborhood of the cement plant, and the lowest – the outermost soils. Similar relation between soil pH and the distance from the cement plant was observed by other authors [11–13]. The change of pH in soils to alkaline range is mostly caused by the dominant component of cement dust – calcium carbonate [14]. The content of calcium carbonate in investigated soils was in the range of 0.38–1.26 % (Table 2). Higher content of calcium carbonate in soil samples was detected in 0–20 cm a layer compared to 20–40 cm layer. The highest content of $CaCO_3$ (1.26 %) was found in the sample from

Zakrucze I, which is located 850 m from the cement plant. The highest content of $CaCO_3$ in the top layer of soil and in the neighborhood of the factory was also observed by other authors [15, 16]. With the increasing distance from the emission source, the $CaCO_3$ content decreased. In the investigated soil samples located closest to the emitter the highest pH and significant additions of $CaCO_3$ was found. A similar relationship between the change of pH and accumulation of $CaCO_3$ content is not confirmed by Dobrzanski et al [14] in their study. Organic carbon content in surface layers ranged from 8.3 to 24.2 $g \cdot kg^{-1}$ and in subsurface layers from 10.3 to 20.3 $g \cdot kg^{-1}$ (Table 2) in studied soils.

Physical and chemical properties of soils, their texture, pH and the content of C-organic have a direct impact on the content of mercury [17].

The total content of mercury in the investigated soils was in range of 12.32–51.6 $\mu g \cdot kg^{-1}$ in surface samples and 7.14–36.30 $\mu g \cdot kg^{-1}$ in subsurface samples (Table 3).The content of this element in surface layers in 83 % (ie 4 samples) of analyzed samples was higher than the content in subsurface layers.

Table 3

Total Hg contents in soils

Sample	Layer [cm]	Hg [$\mu g \cdot kg^{-1}$]
Zakrucze I	0–20	13.00
	20–40	17.28
Zakrucze II	0–20	14.15
	20–40	9.09
Lesnica I	0–20	12.32
	20–40	7.14
Lesnica II	0–20	23.52
	20–40	16.64
Lesnica III	0–20	34.50
	20–40	36.30
Malogoszcz	0–20	51.60
	20–40	31.23

The highest content of mercury was found in surface layer of soil from Malogoszcz – 51.60 $\mu g \cdot kg^{-1}$ and the lowest in subsurface layer of soil from Lesnica I – 7.14 $\mu g \cdot kg^{-1}$. The contamination of soil with mercury on industrial areas concerns mostly the surface layer, because this metal hardly migrates to deeper soil horizons [18]. Similar regularity was found in the investigated soils. This element is not usually washed out to deeper layer of soil, which is related to a large sorption of mercury by soil organic matter [5, 19]. The main factors that increase sorption of mercury are pH and organic matter [19, 20]. The highest content of mercury in the investigated soils corresponded to the high content of C-organic (Table 2 and 3). Natural content of mercury in soils is difficult to determine, but it is assumed it corresponds to a range of 50–300 $\mu g \cdot kg^{-1}$ [7, 20]. Average mercury content in mineral soils does not exceed 100 $\mu g \cdot kg^{-1}$ [7]. The results show that in investigated samples, Hg content was below the average content of this element in non contaminated soils [20]. Similar regularities were observed by Kusza et al [21], who investigated soils formed from chalk marl, which had alkaline pH. Also during the research carried on cultivated soils in the surroundings of "Lafarge" Cement Plant in Bielawy higher total content of Hg in surface layers was observed which could be the result of absorption of this metal by organic substances and clay minerals. Thus, the total content of Hg in soils near Malogoszcz Cement Plant was below the natural, geochemical background level for this element in mineral soils of Poland [13].

Investigated soils poor in soil colloids, were not contaminated with mercury. Thus, Malogoszcz Cement Plant has no significant influence on the total content of mercury in nearby soils. However, elevated level of Hg in surface layers (0–20 cm) compared with subsurface layer (20–40 cm) in the most studied sites is the evidence of some changes in soil environment caused by the dust emission.

Conclusions

1. Physicochemical analysis of soils located in the surroundings of Malogoszcz Cement Plant allow to qualify them as highly vulnerable soils with content of organic carbon in the range of 8.3–24.2 $g \cdot kg^{-1}$ (0–20 layer) and 10.3–20.3 $g \cdot kg^{-1}$ (20–40 layer) and with pH_{H_2O} in the range of 5.66–8.31 (0–20 layer) and 5.61–8.07 (20–40 layer).
2. Emission of cement dusts from Malogoszcz Cement Plant caused the increase of $CaCO_3$ content and the alkalization of soils.
3. Total content of mercury in the analyzed soil material was in range of 7.14–51.6 $\mu g \cdot kg^{-1}$ and in all samples studied did not exceed the content seemed to be natural for this metal.
4. Emission of cement dust from the Lafarge – Cement Plant in Malogoszcz does not cause the increase of total mercury content in the surrounding soils.

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CAŁKOWITA ZAWARTOŚĆ RTĘCI W GLEBACH OKOLIC ZAKŁADÓW CEMENTOWYCH „LAFARGE” W MAŁOGOSZCZY

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Abstrakt: Celem badań było określenie całkowitej zawartości rtęci w glebach sąsiadujących z Zakładem Cementowym „Lafarge” w Małogoszczy. Zakłady są źródłem emisji pyłów cementowych o charakterze alkalicznym. Próbki glebowe pobrano z sześciu punktów z głębokości 0–20 cm i 20–40 cm w różnej odległości od cementowni. Całkowitą zawartość rtęci oznaczono za pomocą spektrometru AMA 254.

Badane gleby można zaliczyć do kategorii gleb lekkich o średniej zawartości C-organicznego. W wyniku przeprowadzonych badań stwierdzono, że próbki gleb w pobliżu źródła emisji wykazują większe wartości pH i zawartości $CaCO_3$. Jest to spowodowane stałą emisją pyłów alkalicznych. Zawartość całkowita rtęci w badanych próbkach glebowych była mniejsza od naturalnej średniej zawartości rtęci w glebach mineralnych Polski. Emisja zanieczyszczeń z Cementowni Małogoszcz nie spowodowała zwiększenia całkowitej zawartości rtęci w badanych glebach.

Słowa kluczowe: pyły cementowe, gleba, rtęć, alkalizacja

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EFFECT OF 40-YEAR DIVERSIFIED FERTILIZER EXPERIMENT ON CHANGES IN MERCURY CONTENT IN GRASSLAND (CZARNY POTOK)

WPŁYW 40-LETNIEGO ZRÓŻNICOWANEGO NAWOŻENIA NA ZMIANY ZAWARTOŚCI RTĘCI W ŚRODOWISKU UŻYTKU ZIELONEGO (CZARNY POTOK)

Abstract: A mountain meadow experiment localized in Czarny Potok village near Krynica (20°54′53″ E; 49°24′35″ N) and conducted since 1968 investigated the effect of diversified fertilization on the content of mercury in soil, meadow sward and applied fertilizers. Soil samples from three horizons of the limed series and the series without liming were analyzed. In the plant and soil material mercury was assessed in the AMA 254 apparatus. Relationships were sought with reference to pH, sulphur and organic carbon.

Long-term fertilization did not diversify mercury contents in the meadow sward, so the most probable agent of the differences between treatments was their botanical composition and the influence of plants on the soil physicochemical properties. Despite a high changeability of the soil pH or sulphur content in the sward, the changeability and content of mercury in the sward were not significantly diversified. Mercury contents in currently used fertilizers are low in comparison with the mercury amounts absorbed by the meadow sward. In spite of a relatively big dose of mercury which may be supplied with calcium fertilizers, no significant effect of liming on the sward mercury contents was registered.

Keywords: long-term fertilizer experiment, mercury, meadow, soil

The year 1989 was accepted in Poland as a referential year in mercury levels assessment because of the highest emission of this element to the environment reaching 39.7 mg Hg [1]. In 2000 the emission was lower by 35 % and in 2005 by 50 % in comparison with the emission in 1989. Despite these changes and dispersion of mercury in the environment, pollution with this element refers in the first place to the elements of the environment. The highest share of mercury load emitted to the atmosphere (60 %) originated from the processes of fuel use for energy generation. The second, after fuel burning, major source of this metal emission are processes of cement manufacturing, in

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which the national emission load constitutes 20 % [2]. Metallic mercury emitted into the atmosphere may cycle in it from 0.5 year to 2 years [3].

Mercury enters waters with precipitations or with groundwater and surface runoffs, however rain and snow play a special role in mercury cycling. Metal release from soil complexes may happen under favourable conditions resulting in their migration to the underground waters.

At the beginning of the eighties of the 20th century it was reported [4] that the hazard of water contamination with heavy metal compounds used in agriculture worldwide was growing particularly with reference to mercury, which was no longer used in fungicides following serious poisonings in humans and animals. Mercury, highly dispersed in water, undergoes the accumulation process, therefore considerable concentrations of this element are sometimes registered in bottom sediments of reservoirs and watercourses [5, 6].

According to Filipek [7] a potential contamination of agrosystems with mercury is relatively weak and occurs only when phosphorus fertilizers manufactured of phosphorites originating from some deposits are used. Higher contents of mercury were noted in soil even to the depth of 60 cm in the vicinity of plants manufacturing phosphorus fertilizers in Brazil [8]. According to Olendrzynski et al [2] no mercury emission is noted during phosphorus fertilizers production and their contents of this element are from 0.01 to 1.2 mg Hg $\cdot$ kg^{-1} [9]. Much bigger mercury amounts were registered in nitrogen fertilizers (0.3–3 mg Hg $\cdot$ kg^{-1}) which was connected with waste utilization for these fertilizers manufacturing (waste ammonium sulphate). Currently admissible value of pollutants in organic and mineral fertilizers plant support products of mineral origin cannot exceed 2 mg Hg per 1 kg on fertilizer or plant support product weight [10]. In comparison with the year 2001, when the regulations governing fertilizers use were standardized, the criterion of mercury concentrations was significantly aggravated. At that time admissible value of pollutants in organic and organo-mineral fertilizers could not exceed 3 mg of mercury per 1 kg and in mineral fertilizers, except calcium and calcium-magnesium fertilizers, 10 mg of mercury per 1 kg of fertilizer mass [11].

In agriculture a source of mercury pollution may be sewage sludge. Sewage sludge produced in the eighties according to Strzelczuk-Ogulewicz [12] contained from 0.1 to 8.2 mg Hg $\cdot$ kg^{-1}, but Filipek [7] reports a wide range of the contents from 0.1 to 55.0 mg Hg $\cdot$ kg^{-1}. It evidences a greater potential of present ploughland contamination with this element in case of uncontrolled use of sewage sludge in agriculture. The permissible content in sewage sludge used for agricultural purposes is 16 mg Hg $\cdot$ kg^{-1} [13].

Kucharzewski et al [14] report a regional diversification of mercury content in agricultural products and its definitely bigger amounts in grasses than in cereal grain. Mercury contents in meadow sward of 48 grasslands from the Lower Silesia region were from 0.0051 to 0.0203 mg Hg $\cdot$ kg^{-1}, but the arithmetic means from three regions fluctuated within a narrow range from 0.0119 to 0.0148 mg Hg $\cdot$ kg^{-1}.

Regulations [15, 16] determine the permissible mercury contents in animal feeds. In feed materials mercury content cannot exceed 0.1 mg Hg $\cdot$ kg^{-1}, except:

- feed obtained from fish, fish processing or other marine animals (to 0.5),
- calcium carbonate (to 0.3).

The aim of presented experiments was to determine the effect of cultivation measures on grasslands, mainly permanent fertilization and liming on mercury concentrations is soil and meadow sward under conditions of long-term fertilizer experiment on a mountain grassland in Czarny Potok. The conditions which formed during the 40-year experiment might have influenced mercury cycling in agrocenosis.

Material and methods

The experiment has been localized in Czarny Potok near Krynica (20°54′53″ E; 49°24′35″ N) at the altitude of about 720 m a.s.l., at the foot of Jaworzyna Krynicka Mt. in the south-eastern massif of the Beskid Sadecki Mts., on the slope with 7° inclination and NNE exposition. The experiment was set up in 1968 on a natural mountain meadow of *Nardus stricta* L. and *Festuca rubra* L. type with a considerable share of the dicotyledonous. The soil from the experimental area was classified to acid brown soils, formed from the Magura sandstone with granulometric composition of light silt loam (with the following share of fractions: 1–0.1 mm: 40 %, 0.1–0.02 mm: 37 %, > 0.02 mm: 23 %) and characteristic three genetic horizons: AhA (0–20 cm – humus horizon), ABr (21–46 cm – browning horizon) and BbrC (47–75 cm parent rock). Details concerning the experiment were presented in a previous paper [17] and in Fig. 1.

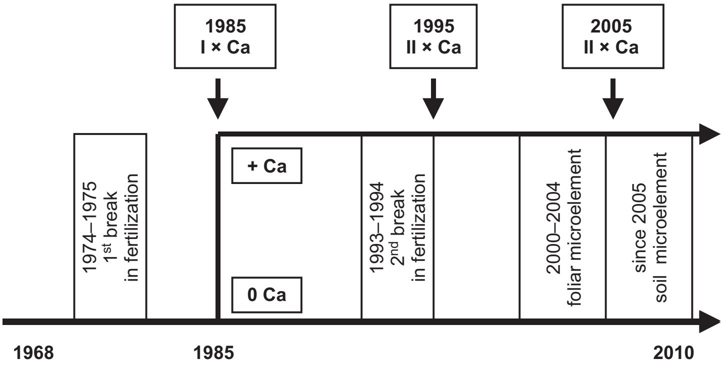

Fig. 1. Scheme of modification of treatments in the experiment

Since autumn 1985 the experiment, at the same doses of the elements, has been conducted in two series: limed and without liming. In 1995 and 2005 liming was repeated. The first and third liming were conducted using a lime dose computed on the basis of 0.5 Hh value, the second considered the total hydrolytic acidity.

In the years 1974–1975 and 1993–1994 breaks were made in mineral fertilization and the experiment was limited to determining the sward yield and its chemical composition.

The experiment, conducted in 5 replications comprises 8 fertilizer treatments (Table 1) on which unilateral nitrogen or phosphorus fertilization (90 kg N or 90 kg $P_2O_5 \cdot ha^{-1}$) against PK background (90 kg $P_2O_5 \cdot ha^{-1}$ and 150 kg $K_2O \cdot ha^{-1}$) and nitrogen in two forms (ammonium nitrate and urea) and in two doses (90 and 180 kg N · ha^{-1}) has been conducted.

Table 1

Scheme of fertilization in static experiment in Czarny Potok

Fertilising objects	Annual dose of the element in series 0 Ca and + Ca (1985, 1995, 2005) [kg · ha^{-1}]			Nitrogen form	Microelements
	P	K	N		
PK	39.24	124.5	—		B; Cu, Zn, Mn, Co, Mo
PK + N	39.24	124.5	90	ammonium nitrate	B; Cu, Zn, Mn, Co, Mo
PK + N	39.24	124.5	180	ammonium nitrate	B; Cu, Zn, Mn, Co, Mo
PK + N 0 microel.	39.24	124.5	90	urea till 2004/ ammonium nitrate from 2005	0 microel.[a]
PK + N 0 microel.	39.24	124.5	180	urea till 2004/ ammonium nitrate from 2005	0 microel.
N	—	—	90	ammonium nitrate	B; Cu, Zn, Mn, Co, Mo
P	39.24	—	—		B; Cu, Zn, Mn, Co, Mo
"0"	—	—	—		B; Cu, Zn, Mn, Co, Mo

[a] 0 microel. – (without microelements); P = 90 kg P_2O_5, K = 150 kg K_2O/ha; 0 Ca unlimed series; + Ca limed series.

In 1968–1980 phosphorus and potassium fertilizers were sown in autumn. Since 1981 the fertilizers have been sown in spring and potassium (1/2 of the dose) has been supplemented in summer after I cut. In the years 1968–1973 calcium thermophosphate (superthomasine) was used, since 1976 triple superphosphate (46 %) and since 2005 enriched superphosphate (40 %) have been applied. During the entire period of the experiment nitrogen fertilizers have been sown at two dates: 2/3 of the annual dose in spring when the vegetation started and 1/3 of the dose about two weeks after I cut. In 1994 a regenerative fertilization was applied with 10 kg Cu and 8 kg Mg · ha^{-1}. In the years 2000–2004 foliar fertilization was conducted (twice 2 dm^3 · ha^{-1}) with microelement Mikrovit-1 fertilizer. The fertilizer contained in 1 dm^3: 23.3 g Mg, 2.3 g Fe, 2.5 g Cu, 2.7 g Mn, 1.8 g Zn, 0.15 g B and 0.1 g Mo. In the 2005–2007 period 0.5 g B per 1 h was supplied to the soil every year, whereas in the spring 2008, 5 kg Cu, Zn and Mn and 0.5 kg of Co and Mo were added per one hectare.

Vegetation period in the experimental area lasts from April to September (150–190 days). Meteorological conditions (Table 2) on the terrain where the experiment is situated indicate a considerable changeability of precipitations.

The research results presented in this paper were obtained from the soil and plant material collected in 2008 (41st year of the experiment) and from analyses performed at the same time on the archival fertilizer samples. Analysis of mercury content was conducted in two replications whereas the soil and plant material were analyzed in 2008 in each replication of individual fertilizer treatments (series · fertilization · replication = = 80 samples/1 cut or soil horizon).

Table 2

Parameters of statistical schedule of precipitation and temperatures for period 1968–2008

Parameter	Precipitation [mm]		Temperature [^{o}C]	
	I–XII	IV–IX	I–XII	IV–IX
Arithmetical mean	876.4	568.5	5.86	12.19
Standard deviation	198.7	138.0	0.87	0.77
Range 25–75 % of cases	733.2–990.0	461.5–658.2	5.35–6.30	11.7–12.7

Soil samples for the analysis were collected from treatments after II cut harvesting from the 0–10 cm, 10–20 cm and 20–50 cm horizons. Yields of green meadow sward mass were determined twice a year: I cut was gathered at the turn of June and July and II cut at the beginning of September.

Mercury was assessed in the plant material on AMA 254 apparatus in which it is released from the amalgamator and measured using atomic absorption at the wavelength 254 nm at the limit of quantification 0.00001 mg of mercury in the assessed sample.

Standard methods were used to determine physicochemical properties of soil: pH was assessed in water solution and 1 mol $\cdot$ dm^{-3} KCl solution by potentiometer, organic carbon by means of the chromate method and total sulphur in plant was determined using ICP–AES method after previous sample mineralization in concentrated nitric acid and magnesium nitrate.

Results and discussion

Toxic effect of mercury is associated with this element ability to form combinations with sulfhydryl or amine groups, or with aminoacids and concerns mainly blocking their biochemical functions. Most probably a major amount of mercury absorbed by roots is bound by sulphur and does not move to plant aerial parts. However, mercury level in pollen obtained by stationary bee-yards situated in two localities near Wroclaw: agro-forest site and former military airport remained considerably higher than in the adjacent region (10–15 km north of the airport), although the airport has been closed for almost 15 years [18].

Mercury contents (Table 3) assessed in the sward from the experiment in Czarny Potok did not differ much from the values registered in other experiments [19, 20].

In 2008 mercury contents in the sward from I cut ranged, respectively from 0.0143 to 0.0236 mg Hg $\cdot$ kg^{-1} in the series without liming and from 0.0120 to 0.0217 mg Hg $\cdot$ kg^{-1} in the limed series (Table 3). Analysis of variance did not reveal any significance of differences between the series, therefore it has been not presented in the paper. Fertilization did not have any marked effect on the sward mercury concentrations, either. Differences in its content in sward from individual treatments were not unanimous, which suggests the influence of some other factors. Mercury contents in the sward from II cut in 2008 was slightly more diversified and mean content for all limed treatments was by 18.8 % higher than an average content in the sward of the treatments without liming.

Table 3

The yield of dry mass and the content and amount of mercury and sulfur in the sward of two cuts in series with and without liming

Series/cut	Fertilising objects								
	PK	90 kg N + PK	180 kg N + PK	90 kg N + PK; 0 microel.	180 kg N + PK; 0 microel.	N	P	“0”	arithmetic mean/ coefficient of variation [%]
[mg Hg · kg^{-1}]									
0 Ca I cut	0.0236	0.0173	0.0186	0.0166	0.0182	0.0143	0.0149	0.0146	0.0173/17.6
0 Ca II cut	0.0169	0.0170	0.0113	0.0182	0.0163	0.0234	0.0177	0.0156	0.0170/19.6
+ Ca I cut	0.0136	0.0217	0.0187	0.0164	0.0173	0.0184	0.0122	0.0120	0.0163/21.1
+ Ca II cut	0.0143	0.0219	0.0221	0.0179	0.0207	0.0266	0.0242	0.0137	0.0202/22.6
[mg S · kg^{-1}]									
0 Ca I cut	1.80	1.40	1.70	1.20	1.40	1.90	2.30	2.02	1.715/21.4
0 Ca II cut	1.90	1.80	1.80	1.60	1.60	2.20	2.70	2.61	2.026/21.3
+ Ca I cut	1.70	1.40	1.70	1.10	1.10	2.10	2.20	2.16	1.683/26.9
+ Ca II cut	1.70	1.80	1.50	1.40	1.40	1.90	2.30	2.61	1.826/23.9
[Mg d.m. · ha^{-1}]									
0 Ca I cut	3.76	4.20	4.17	4.39	5.01	1.77	2.07	2.54	3.489/33.8
0 Ca II cut	2.24	2.17	2.66	2.45	3.08	1.20	0.96	1.20	1.995/39.0
+ Ca I cut	3.74	4.87	5.02	4.20	5.09	2.35	1.89	1.90	3.633/38.4
+ Ca II cut	2.19	2.65	2.73	2.63	2.37	1.42	0.99	1.07	2.006/36.4
[mg Hg · ha^{-1}]									
0 Ca I cut	88.7	72.7	77.6	72.9	91.2	25.3	30.8	37.1	62.04/43.0
0 Ca II cut	37.9	36.9	30.1	44.6	50.2	28.1	17.0	18.7	32.94/35.6
+ Ca I cut	50.9	105.7	93.9	68.9	88.1	43.2	23.1	22.8	62.08/51.6
+ Ca II cut	31.3	58.0	60.3	47.1	49.1	37.8	24.0	14.7	40.29/40.3
[g S · ha^{-1}]									
0 Ca I cut	6768	5880	7089	5268	7014	3363	4761	5130	5659/22.8
0 Ca II cut	4256	3906	4788	3920	4928	2640	2592	3132	3770/23.9
+ Ca I cut	6358	6818	8534	4620	5599	4935	4158	4104	5641/27.1
+ Ca II cut	3723	4770	4095	3682	3318	2698	2277	2793	3419/23.9

The long-term fertilization stabilized botanical composition of the sward [21]. Botanical diversification depends mainly on soil abundance and its pH. It is difficult to seek higher mercury concentrations in the experiment at a bigger share of the dicotyledonous, which usually accumulated greater amounts of heavy metals. Presented fractional compositions (Table 4) refers to I cut sward, however characteristic is the higher content of mercury in the sward of II cut of limed series. This cut yield makes up 1/3 of the yearly yield and is characterized by a bigger share of the dicotyledonous plants on a majority of fertilizer treatments [17]. Diversified yields on the experimental treatments caused different mercury removal. The lowest amounts of mercury taken up with the yield were noted on the treatments without fertilization and with unilateral fertilization. Differences between cuts and series concerning the amounts of absorbed mercury were noted in the year of the experiment on fertilized NPK treatments. Average quantities of mercury removed with the yield from 4 NPK fertilized treatments in I cut were, respectively 78.6 mg in the series without liming and 89.12 mg Hg · kg^{-1} d.m. in the limed series, and in II cut, respectively 40.4 and 53.6 mg Hg · kg^{-1} d.m. The values (Table 3) indicate greater amounts of mercury absorbed by the sward of limed treatments fertilized with ammonium nitrate during the whole period of experiment.

Table 4

Share [%] of botanical fractions in the meadow sward (2002–2003) [21]

Item	Fertilising objects							
	PK	90 kg PK + N	180 kg PK + N	90 kg PK + N 0 microel.	180 kg PK + N 0 microel.	N	P	“0”
	0 CaO							
Grasses	62.0	67.0	89.0	81.0	75.0	52.0	53.0	56.0
Papilionaceae	10.0	0.0	0.0	2.0	0.0	9.0	8.0	4.0
Herbs and Weeds	28.0	33.0	11.0	17.0	25.0	39.0	39.0	40.0
+ CaO								
Grasses	92.0	61.0	60.0	67.0	77.0	59.0	44.0	57.0
Papilionaceae	5.0	0.0	0.0	3.0	1.0	5.0	5.0	2.0
Herbs and Weeds	3.0	39.0	40.0	30.0	22.0	36.0	51.0	41.0

Relatively, within the fertilizer treatments, the quantity of sulphur absorbed by Ist cut sward was not significantly diversified in comparison with the amount of mercury uptake. In case of NPK fertilized treatments the amounts of sulphur uptake fluctuated from 5268 to 7089 g S · ha^{-1} in the series without liming and from 4788 to 8534 g S · ha^{-1} in the limed series. S:Hg ratio should be emphasized, which generally was below 100 on treatments receiving NPK fertilizers and over 100 in case of simplified fertilization or the lack of it. It may evidence mercury dilution in the yield from treatments stimulated by full NPK fertilization.

The highest mercury concentrations were registered in the surface horizon (0–10 cm). In the deeper horizons mercury concentrations were decreasing. The changes were most visible between the 10–20 and 20–50 cm horizons. For both series in the 20–50 cm horizon mercury content was between 65.2 and 69.3 % of the contents from 0–10 cm horizon and between 69.2 and 77.5 % of the 10–20 cm horizon content. Statistically significant differences were also registered between the analyzed 0–10 cm and 10–20 cm horizons. No notable effect of either fertilization or liming on mercury content in soil was found.

Slightly bigger mercury contents were noted in the soil of the 10–20 cm layer of the fertilized treatments in comparison with the treatment without fertilization.

Changes of air and water conditions in soils cause mercury transformations of mercury forms. In her pot experiment Florencka [19] demonstrated a fast rate of mercury content decreasing in soils polluted with this element. Distribution of mercury compounds in soils depends mainly on oxydation-reduction conditions. Mailainen et al [22] revealed the influence of precipitations on mercury leaching from the upper soil profiles. A considerable changeability of precipitations in the experimental area (Table 2) may determine mercury forms availability to plants and this element uptake by plants. As a result of microbiological or chemical mercury methylation processes in soil, each of its form may become available to plants, but it is considered that despite vapours volatility, the process of mercury migration from soils is limited.

Mercury vapours are easily absorbed by both soil organic substance and clay minerals. The main factors increasing mercury sorption are: acidity (the best binding at pH 3–5) and organic substance, which in acid soils increases and in alkaline decreases the quantities of bound mercury [22]. In the discussed experiment the changes in mercury content between respective soil layers and treatments are conditioned by organic carbon contents and soil pH (Table 5), but most probably also by humus quality.

Other investigations conducted on the discussed experiment revealed that diversified botanical composition modifies also the runoff amount [23]. The amount of runoff in individual years or periods depended mainly on precipitations, applied fertilization and period of measurements. Therefore, larger runoffs were observed on the treatments where turf loosening occurred.

Table 5

The content of mercury and organic carbon and pH in three soil layers in series with and without liming

Series	Fertilising objects								
	PK	90 kg N + PK	180 kg N + PK	90 kg N + PK; 0 microel.	180 kg N + PK; 0 microel.	N	P	“0”	arithmetic mean
[mg Hg · kg^{-1}]									
0 Ca 0–10 cm	0.0750	0.0730	0.0740	0.0710	0.0730	0.0780	0.0750	0.0680	0.0733c*
0 Ca 10–20 cm	0.0681	0.0665	0.0700	0.0669	0.0702	0.0693	0.0632	0.0661	0.0690b
0 Ca 20–50 cm	0.0542	0.0455	0.0448	0.0478	0.0443	0.0480	0.0475	0.0506	0.0478a
+ Ca 0–10 cm	0.0770	0.0770	0.0720	0.0720	0.0720	0.0790	0.0730	0.0710	0.0741c
+ Ca 10–20 cm	0.0673	0.0632	0.0612	0.0698	0.0633	0.0724	0.0610	0.0721	0.0663b
+ Ca 20–50 cm	0.0512	0.0467	0.0504	0.0481	0.0496	0.0579	0.0532	0.0537	0.0514a
[g C · kg^{-1}]									
0 Ca 0–10 cm	24.92	25.12	22.90	25.14	23.27	27.44	25.30	24.00	24.76d
0 Ca 10–20 cm	10.88	11.91	10.99	11.45	10.32	11.25	11.91	12.06	11.35b
0 Ca 20–50 cm	7.46	5.31	7.06	6.66	7.98	6.86	6.83	6.70	6.86a
+ Ca 0–10 cm	26.62	26.19	25.45	26.19	25.40	26.90	25.69	28.71	26.39d
+ Ca 10–20 cm	13.83	12.99	13.75	14.43	13.77	13.86	13.38	15.84	13.98c
+ Ca 20–50 cm	7.53	8.86	6.28	6.61	6.02	7.14	6.83	6.21	6.94a

Table 5 contd.

Series	Fertilising objects								
	PK	90 kg N + PK	180 kg N + PK	90 kg N + PK; 0 microel.	180 kg N + PK; 0 microel.	N	P	“0”	arithmetic mean
pH_{KCl}									
0 Ca 0–10 cm	4.11	4.36	3.98	4.35	3.96	4.26	4.66	4.53	4.26a
0 Ca 10–20 cm	3.94	4.12	3.92	4.22	4.06	3.98	4.35	4.35	4.12a
0 Ca 20–50 cm	5.33	5.76	5.28	5.89	5.22	5.19	5.87	5.48	5.50d
+ Ca 0–10 cm	5.45	5.58	5.07	5.42	5.29	5.15	4.42	5.29	5.34c
+ Ca 10–20 cm	4.90	4.84	5.01	5.16	5.00	4.94	4.99	5.17	4.49b
+ Ca 20–50 cm	5.53	5.64	5.92	6.07	5.70	5.81	5.78	5.82	5.78e

* Variance analysis according to Fishera $p < 0.05$.

Mazurek and Wieczorek [20] proved that lower content of mercury in brown soil occurs at higher hydrolytic acidity, bigger organic carbon content, CEC (*Cation-Exchange-Capacity*) and contents of < 0.02 mm fraction. Some of these parameters were confirmed by Rodrigues et al [3] based on 624 soil samples from northern Spain.

Mercury contents were analyzed in archival samples of fertilizers applied in the discussed experiment.

Among the analyzed fertilizers the highest content of mercury (Table 6), which fell within the limits stated by Filipek [7], was assessed in phosphorus fertilizers. Mercury contents assessed in potassium salts and nitrogen fertilizers were lower than quoted by Filipek [7].

Table 6

Range of mercury content [mg Hg $\cdot$ kg^{-1}] in applied fertilizers in 1970–2008 and arithmetic mean of the element amount introduced with fertilizers on 1 ha

Item	Number of investigated fertilizers	Range [mg $\cdot$ kg^{-1}]	Mean [mg $\cdot$ kg^{-1}]	Estimated amount of Hg introduced with fertilizers yearly [mg $\cdot$ ha^{-1}]
Triple superphosphate	5	0.0118–0.0599	0.0333	6.456
Calcium thermophosphate	1		0.0166	5.976
Ammonium nitrate	6	0.0039–0.0191	0.0104	2.753/5.506^{a}
Urea	2	0.0029–0.0030	0.0029	0.567/1.134
Potassium salt^{b}	11	0.0075–0.0407	0.0162	4.860
Calcium fertilizer	2	0.0116–0.0189	0.0153	76.5–160.6^{c}

^{a} Dose of 90 kg N /180 kg N $\cdot$ ha^{-1}; ^{b} with a different K_2O content; ^{c} the range depends on different soil acidification on particular objects.

Because of calcium fertilizer doses, the biggest amounts of mercury supplied to the soil with these fertilizers, depending on the acidity they fluctuated from 76.5 to 160.6 mg

Hg · ha^{-1}. Estimated quantity of mercury absorbed by the meadow sward per hectare (Table 3) is significantly smaller than the amount of mercury supplied to the soil with nitrogen, phosphorus or potassium fertilization.

Conclusions

Long-term fertilization did not diversify mercury contents in meadow sward and the most likely factor of changes in the contents between treatments was their botanical composition and plant influence on soil physicochemical properties.

In spite of considerable changeability of soil pH or sulphur contents in the sward, changeability and contents of mercury in the sward were not significantly diversified.

Mercury contents in currently used fertilizers are small in comparison with mercury amount taken up by the meadow sward.

Despite a relatively big dose of mercury which may be supplied with calcium fertilizers, no marked effect of liming on mercury contents in the sward was registered.

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WPŁYW 40-LETNIEGO ZRÓŻNICOWANEGO NAWOŻENIA NA ZMIANY ZAWARTOŚCI RTĘCI W ŚRODOWISKU UŻYTKU ZIELONEGO (CZARNY POTOK)

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Abstrakt: W górskim doświadczeniu łąkowym zlokalizowanym w Czarnym Potoku koło Krynicy ($20^{o}54'53''$ E; $49^{o}24'35''$ N) prowadzonym od 1968 r. badano wpływ zróżnicowanego nawożenia na zawartość rtęci w glebie, runi łąkowej i stosowanych nawozach. Analizowano próbki glebowe z trzech poziomów 0–10 cm, 10–20 cm i 20–50 cm z serii wapnowanej i bez wapnowania. Rtęć w materiale roślinnym i glebowym oznaczono za pomocą aparatu AMA 254. Poszukiwano zależności w odniesieniu do pH, siarki i węgla organicznego.

Długotrwałe nawożenie nie zróżnicowało zawartości rtęci w runi łąkowej, a najbardziej prawdopodobnym czynnikiem różnic międzyobiektowych w zawartości był ich skład botaniczny i wpływ roślin na właściwości fizykochemiczne gleby. Pomimo dużej zmienności odczynu gleby czy zawartości siarki w runi, zmienność i zawartość rtęci w runi nie były znacząco zróżnicowane. Zawartość rtęci w obecnie stosowanych nawozach jest mała w porównaniu do ilości pobieranej rtęci przez ruń łąkową. Mimo względnie dużej dawki rtęci, która może być wprowadzona z nawozami wapniowymi, nie stwierdzono znacznego wpływu wapnowania na zawartość rtęci w runi.

Słowa kluczowe: długotrwałe doświadczenie nawozowe, rtęć, ruń, gleba

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INFLUENCE OF SELECTED INSECTICIDES ON VERMICOMPOSTING OF WASTES WITH PARTICIPATION OF THE EARTHWORM *Dendrobaena veneta*

WPŁYW WYBRANYCH INSEKTYCYDÓW NA WERMIKOMPOSTOWANIE ODPADÓW Z UDZIAŁEM DŻDŻOWNICY *Dendrobaena veneta*

Abstract: The studies concerned the possibility of vermicomposting organic wastes separated from kitchen wastes. Vermicomposting was conducted with the presence of the earthworm *Dendrobena veneta*. The occurrence of dipteran *Sciaridae* was reduced by application of Nomolt 150SC, Dimilin 25WP and Dar 2.5GR preparations into the substrate (in environmentally safe doses recommended by the producers). The aim of the studies was to determine the influence of these preparations on *D. veneta* characterististics and also on the rate of vermicomposting. The nutritional value of the vermicomposts produced was also recognized.

During 3-months of vermicomposting, no influence of Nomolt 150SC and Dimilin 25WP on earthworms was found. Dar 2.5GR brought about a significant increase in the number and biomass of cocoons laid by earthworms. The rate of vermicomposting did not depend on the presence of insecticides. The characteristics of the vermicomposts produced were as follows: pH in H_2O (min. 6.2–max 6.3); salt concentration (min. 3.9–max 4.1 g NaCl $\cdot$ dm^{-3}), abundance of phosphorus (min. 175–max 193 mg $\cdot$ dm^{-3}); potassium (min. 1267–max 1395 mg $\cdot$ dm^{-3}); calcium (min. 2418–max 2561 mg $\cdot$ dm^{-3}) and magnesium (min. 265–max 278 mg $\cdot$ dm^{-3}) and did not differ. Comparing the content of vermicomposts with the addition of insecticides in nitrate nitrogen to its content in the vermicompost from the control containers, a substantially higher content was indicated in the vermicompost produced by the largest population in contact with Dar 2.5GR.

Keywords: earthworm *Dendrobena veneta*, ecological box, Nomolt 150SC, Dimilin 25WP, Dar 2.5GR, vermicompost characteristics

Since the second half of the 20th century, constant disturbance of mechanisms vital for maintaining an ecological balance have been noticed. There has been a rapid increase in emission of pollution of all environmental resources. The major causes of this phenomenon can be ranked as rapid industrialization, dramatic rising of traffic

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congestion, high level of urbanization, common use of chemicals and inappropriate waste management [1].

Kitchen wastes usually contain about 50 % of biodegradable elements. Acting pro-environmentally, they should be separated from the main stream of municipal wastes, so than they can be composted, subjected to fermentation or vermicomposted [2–8].

Vermicomposting of kitchen wastes can also proceed *on-site*, in earthworm ecological boxes (in Polish conditions described concerning to use the species *Eisenia fetida* (Sav.)) [9–11]. An ecological box constitutes an innovative pro-environmental solution of managing organic wastes *on-site*, but it can become bothersome due to adult forms of *Diptera* of the *Sciaridae* family and its larvae, competing with earthworms over organic wastes [12]. Effective ways for limiting the number of *Sciaridae* in ecological boxes are required.

The aim of the research was to determine the influence of preparations used to suppress *Diptera* (insecticides: Nomolt 150SC, Dimilin 25WP and Dar 2.5GR, in concentrations recommended by the producers as safe for the environment) on number, biomass and reproduction characteristics of the earthworm *Dendrobaena veneta* Rosa 1893. The rate of vermicomposting of kitchen organic wastes and characteristics of vermicompost produced, were also recognized.

Material and methods

The studies were conducted in a constant temperature room (ambient temperature was 20 °C), according to the scheme in Table 1.

Table 1

Plan of the kitchen wastes vermicomposting

Pot	Stratification layer	Waste vermicomposted	Basic population of *D. veneta* [g ± SD][b]	Insecticide[c]
1–3	2 dm^3 of soil[a]	600 cm^3 of kitchen organic waste and 300 cm^3 of cellulose	10 ind. [14.910 ± 0.189]	Nomolt150SC
4–6			10 ind. [14.599 ± 0.169]	Dimilin 25WP
7–9			10 ind. [14.752 ± 0.287]	Dar 2.5GR
10–12			10 ind. [14.359 ± 0.425]	Control

[a] The composition of stratification layer (universal medium for ornamental plants Floro-hum: highmoor peat, lowmoor peat, pearlite, sand, microelements, mineral fertilizer NPK) at the beginning of the experiment; [b] SD – standard deviation; [c] in doses conformable to instruction of the producer.

In the containers, sized 21 · 15 · 10 cm, constant humidity (about 70 %) was maintained following the standard [13]. The stratification layer in the containers characteristics was as follow: pH in H_2O – 6.2; salt concentration – 0.5 g NaCl · dm^{-3}, the concentration of nitrate nitrogen – 1.75 mg · dm^{-3}; available phosphorus – 63 mg · dm^{-3}; potassium – 186 mg · dm^{-3}; calcium – 1027 mg · dm^{-3} and magnesium – 141 mg · dm^{-3}.

Vermicomposted waste mass consisted of 150 cm^3 residues of boiled pasta, bread, potato and apple peelings (in total 600 cm^3 of waste) mixed with 300 cm^3 of cellulose (fragmented egg packaging), introduced to improve conditions of vermicomposting [10]. In order to check the possibility of using the insecticides limiting the occurrence of dipteran *Sciaridae* in ecological boxes, the following preparations were added once into the vermicomposted wastes mass: Nomolt 150SC (in dose of 5 $cm^3 \cdot m^{-2}$, active substance teflubenzuron), Dimilin 25WP (in dose of 4 $g \cdot m^{-2}$, active substance diflubenzuron) and Dar 2.5GR (in dose 400 $g \cdot m^{-2}$, active substance chlorfenvinfos).

The number and biomass of earthworms and cocoons were checked every two weeks during a period of three months vermicomposting (the whole volume of containers was searched by hand).

Mean daily rate of wastes vermicomposting (cm^3 per day) was calculated due to their separation from the stratification layer (the wastes were placed in nylon nets with meshes enabling the earthworms to have an easy access). The rate of wastes transformation into vermicompost was determined repeatedly (during each inspection of the state of earthworm population), by measuring the volume of untreated wastes.

The results obtained were transformed into the volume of the processed residues according to the following formula:

$$a_t = 900 - b_t$$

where: a_t – the volume of the residues processed at the consecutive checkings,
b_t – the volume of the unprocessed residues.

Before determining the characteristics of the vermicomposts produced, some samples were taken at random (3 from each medium), fragmented, and then mixed. From this prepared volume, research samples were measured out: the pH in water using a potentiometric method and the concentration of salt by a conductometric method [$g\ NaCl \cdot dm^{-3}$] were determined. The content of nitrate-nitrogen was measured using an ionometer and ion-selective electrode; available phosphorus was determined by the vanadic-molybdenic method. The content of available potassium and calcium was determined using a flame photometer, and available magnesium was checked using a spectrophotometer by means atomic absorption [$mg \cdot dm^{-3}$].

The results obtained (shown as average ± standard deviation, $n = 6$), were analyzed by applying an Excel spreadsheet. The mean values were compared by variation method, using T-Tukey's test and Statistica PL programme.

Results

Analyzing the effect of the insecticides used on the earthworm population condition, a different effect of these preparations on number and biomass was found (Table 2). The presence of Nomolt and Dimilin reduced the number and biomass of the mean earthworm population compared with the control, but insignificantly ($p > 0.05$). The presence of preparation Dar 2.5GR affected the earthworms *D. veneta* most favourably, by increasing both their total number and biomass. Statistical analysis of these results did not confirm a significant difference compared to the control ($p > 0.05$).

Table 2

The number and biomass of mean population of *D. veneta* earthworm in contact with insecticides

Parameter	Nomolt 150SC	Dimilin 25WP	Dar 2.5GR	Control
Number [specimen / box]	11 ± 4	10 ± 4	26 ± 28	16 ± 9
Biomass [g]	14.057 ± 2.732	13.425 ± 3.473	22.155 ± 7.630	18.143 ± 6.015

The stress occurred by the presence of insecticide Nomolt 150SC caused the decrease in number and biomass of adult earthworms of *D. veneta* (Table 3). It seems, that their life strategy, in contact with this xenobiotic was being realized through investing energy in the next generation – the earthworms were laying heavier cocoons than in the control treatment (Table 4). Statistical analysis of these results did not confirm a significant difference ($p > 0.05$).

Table 3

Influence of insecticides on number and sum of biomass of mature individuals of *D. veneta*

Parameter	Nomolt 150SC	Dimilin 25WP	Dar 2.5GR	Control
Number [specimen / box]	8 ± 2	8 ± 3	10 ± 1	11 ± 4
Biomass [g]	13.5 ± 2.5	12.9 ± 3.7	18.7 ± 2.3	16.8 ± 4.5

Table 4

Influence of insecticides on the number and sum of biomass of cocoons laid by *D. veneta*

Parameter	Nomolt 150SC	Dimilin 25WP	Dar 2.5GR	Control
Number [cocoons / box]	12 ± 9	9 ± 7	26 ± 22^{a}	10 ± 4^{b}
Sum of biomass [g]	0.315 ± 0.246	0.213 ± 0.166	0.642 ± 0.546^{a}	0.249 ± 0.217^{b}
Biomass of 10 cocoons [g]	0.193 ± 0.122	0.161 ± 0.125	0.165 ± 0.129	0.169 ± 0.132

a, b – mean in columns denoted with identical letters do not differ significantly ($p < 0.05$) according to T-Tukey's test.

The studies may indicate that the earthworm *D. veneta* is most sensitive to contact with Dimilin 25WP preparation. Both; the whole population (Table 2), and mature individuals (Table 3) and cocoons (Table 4) were smallest in number in containers with this xenobiotic. Similar relations concerned biomass characteristics. Using this insecticide in doses recommended by the producer, determined however the fact that statistical analysis of the results obtained did not confirm the significance of differences obtained (compared with the control) ($p > 0.05$).

On the other hand, it seems that Dar 2.5GR was the most favorable of the preparations tested. The stress caused by its presence did not reduce the number and biomass of mean earthworm population (compared with the control) (Table 2), but even significantly increased the number ($p < 0.01$) and total biomass of the cocoons laid ($p < 0.05$) (Table 4).

The studies conducted allowed calculation of mean daily rate of vermicomposting in all the ecological boxes being observed (Table 5). It fluctuated from 22 to 24 cm^3 per day (the highest was found in the boxes containing insecticide Dar 2.5GR). Statistical analysis of the results did not confirm the significance of the difference obtained ($p > 0.05$).

Table 5

Influence of insecticides on a daily rate ± SD of vermicomposting [in cm^3]

Nomolt 150SC	Dimilin 25WP	Dar 2.5GR	Control
22 ± 16	23 ± 21	24 ± 13	22 ± 18

All vermicomposts from the research containers were rich in plant nutrients. Vermicomposting of organic waste enriched them compared with the initial stratification layer respectively: in nitrate-nitrogen by more than ten thousand times, in phosphorus by 290 %, in potassium by 715 %, calcium by 241 % and magnesium by 189 %) (Table 6).

Table 6

Characteristics of produced vermicomposts (determined in fresh mass, at humidity of 70 %)

Characteristics	Initial medium	Agent tested				Optimal value*
		Nomolt 150SC	Dimilin 25WP	Dar 2.5GR	Control	
pH in H_2O	6.2	6.3 ± 0.0	6.3 ± 0.1	6.3 ± 0.1	6.2 ± 0.0	6.0–7.5
Salinity [g NaCl · dm^{-3}]	0.5	4.1 ± 0.0	4.1 ± 4.1	4.1 ± 0.3	3.9 ± 0.2	about 1.0
$N\text{-}NO_3$ [mg · dm^{-3}]	1.8	409^a ± 18	410^a ± 29	518^b ± 33	423^a ± 21	50–120
P [mg · dm^{-3}]	63	175 ± 23	176 ± 10	190 ± 15	193 ± 18	40–80
K [mg · dm^{-3}]	186	1307 ± 54	1350 ± 101	1395 ± 138	1267 ± 73	125–250
Ca [mg · dm^{-3}]	1027	2479 ± 136	2561 ± 35	2418 ± 143	2442 ± 90	1000–2000
Mg [mg · dm^{-3}]	141	258 ± 13	278 ± 32	265 ± 6	265 ± 12	60–120

* The optimal level for garden plants according to Konczak-Konarkowska [14]; [a, b] difference statistically significant ($p < 0.05$).

Comparing the content of nutrients in vermicomposts with xenobiotics with their content in vermicomposts from control containers, only significantly higher content of nitrogen in vermicomposts produced by the largest population in contact with Dar 2.5 GR was noticed. All the obtained media were excessively saline (Table 6).

Discussion

The obtained results of the earthworm *D. veneta* population in contact with the insecticides tested characteristics may indicate relatively good selection (also by the producers of these preparations) of concentrations of the preparations used. The conducted studies and statistical analysis of the results did not confirm the significance of their negative influence on earthworms during the period of three months of vermicomposting. Apart from different resistance to stress caused by the presence of the insecticides being tested, differentiation of the average number and biomass *D. veneta* can be justified by the fact of more or less efficient influence of the preparations used against dipteran *Sciaridae* larvae, competing with earthworms over organic wastes. More efficient restriction of the number of these larvae could enable a better access of earthworms to organic wastes, which alleviate stress more effectively.

In the condition of the conducted experiment, in contact with earthworms *D. veneta*, Dar 2.5GR turned out to be the least harmful. Meanwhile, numerous studies show that earthworm species may differently respond to contact with xenobiotics. It depends, not only on their individual predisposition, but also on a series of biotic and abiotic factors [15–19]. Results from Garczynska's studies on effect of the same preparations in doses indicated by the producers on the earthworm *E. fetida* [20], phosphoorganic preparation Dar 2.5GR, influenced earthworms of this species (smaller than earthworm *D. veneta*) the most negatively.

In variable temperature condition, in a laboratory, its presence determined a significant reduction in biomass of *E. fetida* and negatively influenced the next generation (reduced the number and biomass of the cocoons laid by the earthworms). In the constant temperature room conditions, at 20 ^{o}C, with *E. fetida*, Dar 2.5GR caused even more toxic effects. It resulted in the reduction of the number (by 41 % compared with the control) and biomass of the whole earthworm populations. It significantly reduced the number and biomass of all individual age class representatives (both mature and immature individuals and also cocoons). These facts influenced weakening of the earthworm population's condition and substantial lowering of the daily rate of vermicomposting of kitchen organic wastes, compared with the control [20].

During the current test, positive influence of vermicomposting on the content of nutrients accessible to plants has been indicated. It has been observed that the vermicomposts produced with the participation of earthworms *D. veneta* did not differ in respect of pH (min. 6.2; max 6.3) and salt concentration (min. 3.98; max 4.13) at the same time, the NaCl concentration ($g \cdot dm^{-3}$) exceeded tolerance threshold for plants ($3\ g \cdot dm^{-3}$) [11]. It is worth mentioning that there have already been studies which confirm high salinity of the vermicomposts produced during vermicomposting of kitchen wastes [10, 21].

The vermicomposts obtained now, like the ones obtained in Kiepas-Kokot and Szczech studies [21] were rich in nutrients for plants. They did not differ in respect of the content of phosphorus, potassium, calcium and magnesium. Only the content of nitrate-nitrogen compared with the other variants of the experiment, was considerably higher in ecological boxes with Dar 2.5GR preparation.

Conclusions

1. The separated fraction of organic kitchen wastes can be vermicomposted *on-site* in earthworm ecological box, using the earthworm *Dendrobaena veneta* Rosa 1893. The nuisance concerned with keeping the box caused by the presence of *Sciaridae* can be limited by antidipteran preparations.

2. Among the insecticides being tested, Dar 2.5GR had the most favorable influence, taking density, biomass and reproduction of earthworms *D. veneta* into account.

3. Inserting all the tested insecticides into the ecological box did not differentiate a daily rate of vermicomposting of organic wastes.

4. The vermicomposts produced from organic kitchen waste were rich in nutrient components for plants (nitrogen, phosphorus, potassium, calcium and magnesium). Significantly the largest content of nitrate-nitrogen was found in the vermicompost with the addition of Dar 2.5GR preparation. As the salinity of vermicomposts coming from kitchen wastes exceeded the tolerance threshold for plants and the content of nutrient components was very high, the fertilizers produced should be diluted before inserting them into soil substrates of plants.

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WPŁYW WYBRANYCH INSEKTYCYDÓW NA WERMIKOMPOSTOWANIE ODPADÓW Z UDZIAŁEM DŻDŻOWNICY *Dendrobaena veneta*

Zakład Biologicznych Podstaw Rolnictwa i Edukacji Środowiskowej
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Abstrakt: Badania dotyczyły możliwości wermikompostowania w skrzynkach ekologicznych odpadów organicznych wydzielonych ze strumienia odpadów kuchennych. Wermikompostowanie prowadzono z udziałem dżdżownicy *D. veneta*, a występowanie muchówek *Sciaridae* ograniczano przez stosowanie do podłoży preparatów Nomolt 150SC, Dimilin 25WP i Dar 2,5GR, w bezpiecznych dla środowiska dawkach sugerowanych przez producentów. Celem badań było określenie wpływu tych preparatów na cechy dżdżownic *D. veneta*, a także tempo wermikompostowania odpadów i cechy wyprodukowanych wermikompostów.

W okresie 3 miesięcy prowadzonych badań nie stwierdzono wpływu insektycydów Nomolt 150SC i Dimilin 25WP na dżdżownice, a najkorzystniej oddziaływał na nie preparat Dar 2,5GR (powodował istotny wzrost liczby składanych kokonów i ich biomasy). Tempo wermikompostowania nie zależało od obecności insektycydów. Cechy wyprodukowanych wermikompostów: pH w H_2O (min. 6,2–max 6,3); stężenie soli (min. 3,9–max 4,1 g NaCl $\cdot$ dm^{-3}), zasobność w fosfor (min. 175–max 193 mg $\cdot$ dm^{-3}); potas (min. 1267–max 1395 mg $\cdot$ dm^{-3}); wapń (min. 2418–max 2561 mg $\cdot$ dm^{-3}) i magnez (min. 265–max 278 mg $\cdot$ dm^{-3}) nie różniły się. Porównując zasobność wermikompostów z dodatkiem insektycydów w azot azotanowy z jego zawartością w wermikompoście z pojemników kontrolnych, wykazano istotnie wyższą zawartość tylko w wermikompoście wytworzonym przez najliczniejszą populację w kontakcie z insektycydem Dar 2,5GR.

Słowa kluczowe: dżdżownice *D. veneta*, skrzynka ekologiczna, Nomolt 150SC, Dimilin 25WP, Dar 2,5GR, cechy wermikompostów

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ANALYSIS OF CHEMICAL PROPERTIES OF THE INCINERATION WASTES AND THE POSSIBILITIES OF THEIR BIOLOGICAL RECLAMATION

ANALIZA WŁAŚCIWOŚCI CHEMICZNYCH ODPADÓW PALENISKOWYCH POD KĄTEM ICH BIOLOGICZNEJ REKULTYWACJI

Abstract: The paper presents the results of the studies of chemical properties of the incineration wastes, 8 years after finishing their deposition in the sedimentation pond using the method of hydraulic transportation. The studies referred to 5 horizons of the profile up to the depth of 80 cm and 3 zones systematically distant from the place of the wastes deposition.

The results indicate that within 8 years there was a displacement of a significant amount of components to the deeper layers of the profile, and consequently the decrease in pH and electrolytic conductivity. However, the satisfactory effect such as diminishing the pH value to the level tolerable for the majority of higher plants refers only to layer 0–10 cm in the whole study area and 0–20 cm in the area up to 400 m from the point of discharge. The properties of wastes after 8 years from their deposition in the sedimentation pond do not allow efficient biological reclamation of the object without applying remediation measures.

Keywords: incineration wastes, chemical properties, reclamation

In Poland, the development of coal-based energy industry causes that a large amount of incineration wastes are disposed on the heaps and in sedimentation ponds, the area of which is over 3000 ha [1]. These objects, after finishing their construction, should be immediately subdued to reclamation measures. The most important task is carrying out measures allowing quick introduction of vegetation that would permanently secure the repository from eolic erosion (harmful to the neighbouring areas) and stimulate soil-making processes, and consequently, make the area productive [2–5]. For this purpose,

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different techniques and technologies are applied, such as isolating the surface of the sedimentation pond with soil formations, or the improvement of the properties and enrichment of the ash mass with wastewater sludge [2, 4, 6–8]. Because of technological reasons it sometimes happens that such objects are temporarily not covered by reclamation measures and, despite initially extremely unfavourable chemical properties, after some years the process of their covering with vegetation starts during spontaneous succession [1].

This paper presents the results of studies referring to the chosen chemical properties of incineration wastes in the vertical section of the sedimentation pond and dimension of the sedimentation pond, in terms of their biological reclamation, 8 years after the end of their deposition.

Material and methods

The studies were carried out on the sedimentation pond of the incineration wastes "Czajki II", made in the process of the combustion of hard coal in the cogeneration plant of the Nitrogen Industry Plant *Zakłady Azotowe* (Z.A.) Tarnow-Moscice. This sedimentation pond was located in the hole after gravel exploitation, where initially lime was deposited, and after removing the lime the pond was filled with incineration wastes, which had been hydrotransported there.

The results of the studies carried out in the first year after ending the deposition of wastes on the mentioned above sedimentation pond and some other sedimentation ponds of the cogeneration plant in Moscice, showed clear spatial differentiation of their properties. The grain composition usually corresponded to dust or clay formations with 20–30 % content of colloid silt. They were characterized by low proper and volume density (2.0–2.15 $g \cdot cm^{-3}$ and 0.8–1.2 $g \cdot cm^{-3}$, respectively) and about 50 % general porosity. They showed strongly alkaline reaction (pH 8.8–10.1) and elevated electrolytic conductivity (about 0.9 $mS \cdot cm^{-1}$) [1, 3].

In the studies carried out 8 years from finishing the deposition, chemical properties were analysed in the wastes taken from 5 layers (0–10 cm; 10–20 cm; 20–40 cm; 40–60 cm and 60–80 cm), in three zones of distance from the place of their discharge (250–300 m, 350–400 m and 450–500 m). The samples of the material were analysed with standard laboratory methods. There were the following analyses: pH, electrolytic conductivity (formation: water as 1:5), roasting losses, total N (Kjeldahl method), elements Ca, Mg, K, Na, Fe, P, Zn, Cu, Sr, Pb and Cd extracted in mixture of $HClO_4$ and HNO_3 acids in 4:1 proportion using the AAS method and ions extracted in H_2O: Ca^{2+}, Mg^{2+}, K^+ and Na^+ – using the AAS method, SO_4^{2-} (using the Polish standard PN-79 C-04566), Cl^- (using the PN-ISO 9297) and HCO_3^- (using the PN 90/C 04540/3). To find the statistic significance of the differences in the basic properties of wastes, between the subsequent layers in the vertical section of the sedimentation pond, the assessment of the homogeneity of variance was made by the Levene's test, and then by one-factor analysis of variance and LSD ($\alpha = 0.05$).

Results and discussion

Sedimentation ponds for incineration wastes are objects that are difficult to reclaim biologically, because of some unfavourable physical and chemical properties, first of all strong alkaline reaction of the disposed material. Such formations, despite great general porosity (about 50 %) do not show good aeration, due to the small amount of macropores and small proper density, with a great participation of the dust fraction, which makes them susceptible to eolic erosion [9, 10]. Hydraulic transport and discharge point of a semiliquid mass causes its segregation and significant spatial differentiation of both physical and chemical properties. The carried out studies during first 3 years after ending the deposition of wastes on several ash sedimentation ponds in Z.A. Tarnow, referring to their chemical properties and spontaneous succession of vegetation, indicate that there is a process of the transfer of the components into the profile and slow diminishing of the pH, especially in the surface horizons and subsequent entering of mosses and vascular vegetation tolerating alkaline reaction [1, 3].

The results of the studies carried out 8 years after the end of the waste deposition indicate significant differentiation of the analysed chemical properties both in the profile up to the depth of 80 cm, as well as in space, proportionally to the distance from the point of their hydraulic discharge. The greatest changes occurred in the surface layer of the sedimentation pond, of 10 cm thickness, in which pH of the material was 7.8 and was 0.9 units lower than the reaction recorded 3 years after finishing the construction of the repository [1]. In the vertical section up to the depth of 60 cm there was a growing trend of the pH value, and then its stabilization on the level of 8.8 (Table 1). The differences in pH values of layers 0–10 cm and 10–20 cm were statistically significant (LSD test), as well as between these layers and deeper layers (20–80 cm).

Table 1

Basic chemical properties of incineration wastes 8 years after finishing their deposition in the sedimentation pond

Layer [cm]	Statistical parameter	pH in H_2O	Electrolytic conductivity (EC) [$mS \cdot cm^{-1}$]	$CaCO_3$	Roasting losses in 400 °C
				[%]	
0–10	Mean SD	7.77 0.15	0.193 0.033	1.20 0.37	9.01 1.90
10–20	Mean SD	8.33 0.31	0.212 0.110	2.25 0.82	5.93 3.51
20–40	Mean SD	8.60 0.30	0.356 0.208	1.77 0.25	5.29 1.87
40–60	Mean SD	8.83 0.08	0.517 0.168	1.55 0.53	3.75 0.53
60–80	Mean SD	8.80 0.20	0.491 0.185	1.53 0.29	6.23 4.56
LSD (α = 0.05, n = 6)		0.25	0.144	n.s.	2.85

Mean – Arithmetic mean; SD – Standard deviation; n.s. – not significant differences.

In layer 0–10 cm of the whole sedimentation pond, within 8 years there was a change of reaction from strongly alkaline into slightly alkaline, also in the layers 10–20 cm in the zone up to 400 m from the point of discharge and 20–40 cm, in the zone up to 300 m the value of pH did not exceed 8.5. So it can be regarded that the reaction of the wastes is currently tolerated by many plant species. Compared with the initial state, pH lowered in the whole analysed vertical section, the most in the surface layer (0–10 cm), on aver-

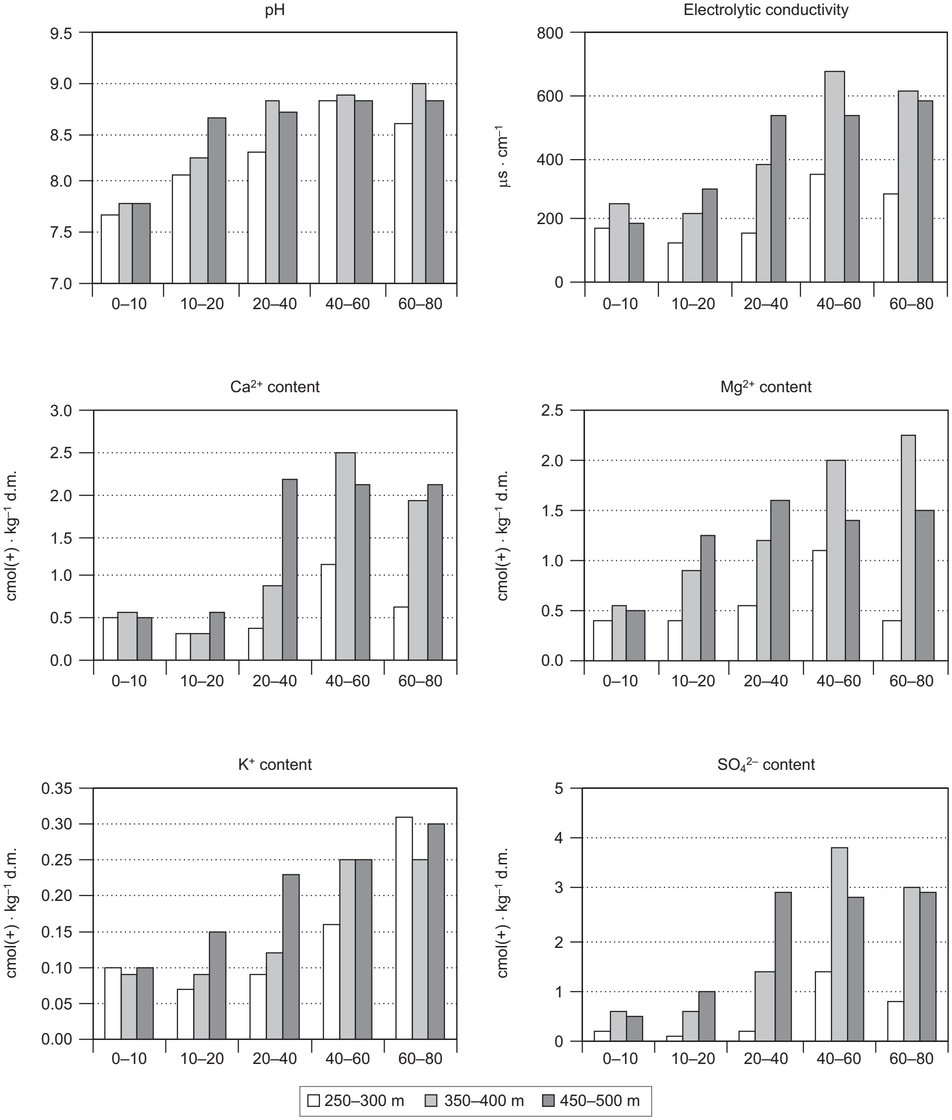

Fig. 1. The formation of selected properties of incineration 8 years after ending their deposition in the sedimentation pond, depending on the distance from the discharge point (water extract)

age more than 1 unit, the smallest decrease was on the depth of 40–80 cm – less than 0.5 unit. A differentiation of this property was also stated in the connection with the distance from the point of the hydraulic discharge of wastes, while the smallest decrease, only 0.3 unit refers to 0–10 cm layer (SD = 0.15), the largest – above 1 unit was found on the depths of 10–20 cm (SD = 0.31) and 20–40 cm (SD = 0.30). The value of pH usually grows with the distance from the point of discharge (Fig. 1).

A similar distribution refers to the values of electrolytic conductivity. The lowest was found in the layer 0–10 cm – 0.19 $mS \cdot cm^{-1}$, with a clearly growing trend down to the depth of the vertical section to 60 cm (the difference between layers 0–10 cm and 10–20 cm from one side and deeper layers from another, was statistically significant). With the growing distance from the point of discharge of wastes it was found that the growth of the value of the electrolytic conductivity in upper layers to the depth of 60 cm (Fig. 1).

The growth trend down the depth of the vertical section was also in case of all the ions analysed in the water's extract (Table 2). The increase of the contents of K^+ and Na^+ with the depth took place in the whole examined vertical section of the decantation pond, while in the case of the content of Ca^{2+}, Mg^{2+} and SO_4^{2-} the growing trend ended on the depth of 60 cm. This indicates that sodium and potassium moves deeper than other analysed ions, which, in large amount, are stopped on the depth of 40–60 cm. The contents of these ions in the vertical section, counted in chemically equivalent units, are many times larger than the contents of K^+ and Na^+. This explains the described distribution of pH and electrolytic conductivity values in the formations of the studied layers, as well as the confirmed during the fieldwork phenomenon of their cementation on the depth of 40–60 cm, also noticed by some authors [1, 6, 10]. It can also be stated that with the growth of the distance from the point waste discharge the content of the ions analysed in water solution grew, however it can be undoubtedly applied only to the range of depth 10–40 cm (Fig. 1).

Table 2

The content of selected ions in water extract in the incineration wastes
8 years after finishing their deposition in the sedimentation pond

Layer [cm]	Na^+	Mg^{2+}	K^+	Ca^{2+}	SO_4^{2-}	Cl^-	HCO_3^-
	[cmol(+) · kg^{-1} d.m.]						
0–10	0.10	0.50	0.10	0.52	0.39	0.09	0.80
10–20	0.09	0.85	0.10	0.43	0.54	0.09	1.00
20–40	0.11	1.12	0.15	1.15	1.50	0.14	1.13
40–60	0.16	1.49	0.19	1.91	2.71	0.08	1.20
60–80	0.22	1.37	0.29	1.55	2.23	0.10	1.20

In other analysed properties similar regularities were not found. The content of $CaCO_3$ is shaped on a close level in the whole profile (1.2 do 2.25 %) slightly higher content was recorded only in horizon 10–20 cm. The losses of roasting are medium for the particular layers in the range 3.75–9.01 %, however they show large differentiation (depending on the horizon V = 21 to 59 %). The largest values were found in horizon 0–10 cm, at relatively low variability (V = 21 %), while the largest differentiations occurred in horizon 10–20 cm (V = 59 %). A similar distribution can be found in the case of total content of N and P in the vertical section of the sedimentation pond (Tables 1 and 3).

Table 3

The total content of macroelements in the incineration wastes
8 years after finishing their deposition in the sedimentation pond

Layer [cm]	Na	Mg	K	Ca	Fe	P	N
	[g · kg^{-1} d.m.]						
0–10	2.88	7.14	5.87	16.09	23.18	2.12	1.09
10–20	2.26	10.40	5.77	18.09	45.10	1.92	0.57
20–40	1.98	8.57	3.90	16.81	35.88	1.45	0.37
40–60	2.38	7.76	4.47	13.04	25.14	1.29	0.32
60–80	2.35	7.77	4.03	14.63	33.71	1.24	0.76

The total content of other macroelements, despite clear differentiation in the profile, do not show clear trends of changes (Table 3). The largest mean content of Ca and Mg was found in layer 10–20 cm, while N, P, K and Na – in a layer 0–10 cm. The differentiation of contents of these components in the connection with the distance from the point of waste discharge is considerable, however only in the case of Ca and Mg in horizons 10–20 cm and 20–40 cm one can state clear growing trend with the distance (Fig. 2).

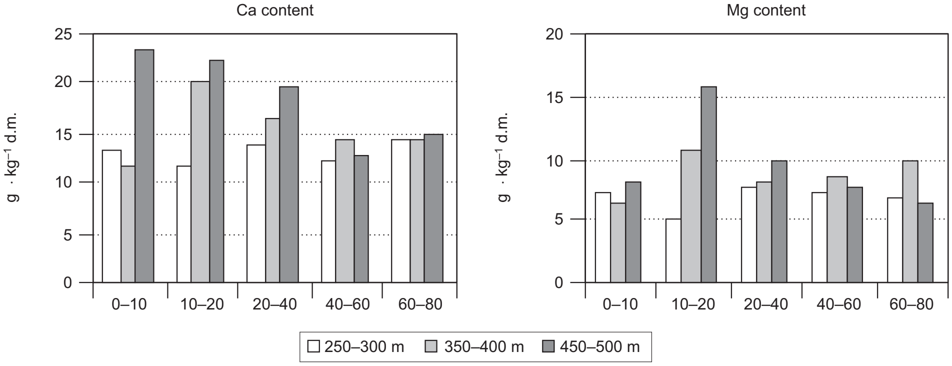

Fig. 2. The formation of general contents of selected elements in the incineration wastes 8 years after ending their deposition in the sedimentation pond, depending on the distance from the discharge point

The results of the determinations of total contents of alkaline elements and their content in the water solution show that their removal resulted in lowering pH and the electric conductivity; this mainly refers to the layers up to 40 cm.

Tabela 4

The total content of selected trace elements in the incineration wastes
8 years after finishing their deposition in the sedimentation pond

Layer [cm]	Cu	Zn	Sr	Cd	Pb
	$[\mathrm{mg \cdot kg^{-1}}$ d.m.]				
0–10	61.50	45.70	61.17	0.31	39.83
10–20	61.33	41.33	48.73	0.25	25.33
20–40	48.33	41.37	38.07	0.23	33.33
40–60	51.17	51.00	37.57	0.32	39.17
60–80	50.00	55.10	34.83	0.33	40.50

The results of the determinations of total contents of trace elements do not show clear trend of the differentiation in the vertical section of the sedimentation pond (Table 4). It can also be stated that the contents of these elements do not exceed threshold values for arable and forest land, defined by the Enactment of the Minister of Environment "referring to the standards of the quality of soil and the quality of ground" (Dz.U. nr 134, poz. 1140).

Conclusions

1. Within the period of 8 years from ending the deposition of incineration of wastes in the sedimentation pond there was a displacement of a significant amount of the components down the deeper layers of the profile, and as a result of this process pH values and the values of electrolytic conductivity of wastes decreased.
2. A sufficient effect such as the decrease of pH values of wastes to the level tolerable by most of plants occurred in layer 0–10 cm in the whole area and in layers 10–20 cm in the zone up to 400 m from the point of discharge and 20–30 cm in the zone up to 300 m.
3. The total contents of macroelements, despite clear differentiation in the vertical section of the sedimentation pond, do not show clear trends of changes. The highest contents of N, P, K and Na were found in the layer of 0–10 cm, while Ca and Mg in the layer of 10–20 cm. With the increase of the distance from the point of wastes disposal, only in case of the content of Ca and Mg in layers 10–20 cm and 20–40 cm; there was a growing trend.
4. The contents of trace elements do not show clear trend of differentiation in the vertical section of the sedimentation pond and stay within the limits defined as acceptable in the standards for soils on arable and forest land.
5. The properties of the incineration wastes after 8 years from their deposition in the sedimentation pond still do not allow efficient biological reclamation of the object without applying remediation measures.

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ANALIZA WŁAŚCIWOŚCI CHEMICZNYCH ODPADÓW PALENISKOWYCH POD KĄTEM ICH BIOLOGICZNEJ REKULTYWACJI

Katedra Kształtowania i Ochrony Środowiska
Akademia Górniczo-Hutnicza w Krakowie

Abstrakt: W pracy zamieszczono wyniki badań właściwości chemicznych odpadów paleniskowych po 8 latach od zakończenia ich składowania w osadniku metodą hydrotransportu. Badania dotyczyły 5 warstw w przekroju pionowym osadnika do głębokości 80 cm i 3 stref systematycznie oddalonych od miejsca zrzutu odpadów.

Uzyskane wyniki wskazują, że w okresie 8 lat nastąpiło przemieszczenie znacznej ilości składników do głębszych warstw osadnika i w konsekwencji zmniejszenie wartości pH i przewodności elektrolitycznej. Jednak wystarczający efekt w postaci zmniejszenia wartości pH do poziomu tolerowanego przez większość roślin wyższych dotyczy tylko warstwy 0–10 cm na całej badanej powierzchni i 0–20 cm w strefie do 400 m od punktu zrzutu. Właściwości odpadów po 8 latach od ich zdeponowania na osadniku nie pozwalają na efektywną rekultywację biologiczną obiektu bez zastosowania zabiegów naprawczych.

Słowa kluczowe: odpady paleniskowe, właściwości chemiczne, rekultywacja

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Krzysztof KUD[1]

INFLUENCE OF ALLUVIAL PROCESSES ON THE CIRCULATION OF MANGANESE AND LITHIUM IN RIPARIAN ENVIRONMENTS

ODDZIAŁYWANIE PROCESU NAMULANIA NA OBIEG MANGANU I LITU W ŚRODOWISKU ŁĘGOWYM

Abstract: Lithium and manganese are indispensable for proper functioning of all living organisms including plants, animals and human beings. However, if these elements occur in excessive amounts, they might prove poisonous. The studies have been carried out on riparian meadows of the San River Valley. The set of research tasks involved examining some stages in the circulation of chemical elements in the environment including alluvial soils, fresh alluvium rejuvenating soil profiles and riparian plant communities.

The results of the studies have confirmed the crucial importance of alluvial processes for lithium and manganese circulation in a riparian environment. These processes could prove useful in the balance of chemical elements as well as in an increase of their availability to plants.

Keywords: alluvial soils, fresh alluvium, heavy metal, manganese, lithium

As a result of water activity river valleys are prone to continuous change. Alluvial valley is the most common variety closely connected with a river activity. Areas adjacent to the flowing bodies of water such as rivers and severely affected by their flow are called riparian zones. These ecosystems occur on lower terraces of stream and river valleys and are annually flooded by swollen waters. When the flood is over, the waters recede leaving behind fertile and drained soil.

Flood waters even after gentle rain become rich in transported suspension and turn into yellow and brown. Carpathian flysh and so the region of the Bieszczady and Lower Beskid mountains may serve as an example [1, 2]. Fresh alluvium deposited by floods was subjected to close examination in the conviction that it may harbour toxic elements.

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The studies were carried out in riparian areas susceptible to periodic flooding and concentrated on the content of biogenic elements present in these environments. This paper presents the content of lithium and manganese in the alluvium-soil-plant system.

Manganese is a biogenic trace element essential for living organisms. It participates in water photolysis reactions and is responsible for forming bridges between ATP particles and thus for energy transfer [3]. Lithium deficiency in mammals results in disruption of protein metabolism and impairs reproductive ability. Lithium preparations are used in the treatment of metal disorders and are proved to exert a beneficial effect on the circulatory system as well as sugar and cholesterol metabolisms [3]. It must be said, though, that large amounts of this element lead to intoxication of living organisms [4]. Excessive concentration of lithium in the environment is a rare occurrence but when it happens it may have serious repercussions on the metabolism of other elements such as copper, phosphorus and iron [3].

Material and methods

The research covered the area of permanent grasslands in the San River Valley from the source to the mouth of the river where it flows into the Vistula River. Large, dense areas of natural grasslands perched on alluvial soils close to the river were selected for investigation. Soil samples were taken from two layers 0–10 cm and 10–30 cm, which correspond to turf and subturf layers, respectively. Prior to soil examination, plants had been sampled from the area of 1 m^2. Fresh alluvium samples were also collected from permanent meadows which are subject to constant alluvial processes. The samples were taken immediately after the waters receded so as to avoid changes in their properties caused by rainfall or biocenosis.

The basic properties of air-dried soil and alluvium samples were determined by means of methods commonly used in chemical and agricultural laboratories [5]. Soil samples were mineralised in 70 % $HClO_4$ in Tecator, a temperature-programmed aluminium block. Then the content of manganese forms was determined following the method of *atomic absorption spectrophotometry* (AAS). The quantitation limit was set at 8.01 $mg \cdot kg^{-1}$ d.m. This method was also used to determine the content of forms soluble in 1 mole $HCl \cdot dm^{-3}$. The measurements were made in the filtrate obtained by shaking the soil samples with one molar solution of HCl for one hour.

Plant material was ground, dried in 70 ^{o}C and then mineralised in a mixture of acids HNO_3, $HClO_4$ and H_2SO_4 in a ratio of 20:5:1, respectively, in an aluminium block. The content of manganese was determined by atomic absorption spectrophotometry.

Results

The basic properties of alluvial soils and fresh alluvium have been presented in Table 1.

The soils had a neutral reaction and quite high contents of calcium carbonate and organic carbon [6]. Granulometric composition of alluvial soils was very diversified.

Considerable differences were observed not only between the examined objects but also within a particular object of research.

Table 1

The basic properties of examined alluvial soils and fresh alluvium of the San River Valley

Property		Arithmetic mean	Geometric mean	Median	Range	
					Minimum	Maximum
Layer 0–10 cm						
Granulometric composition [%]: particle diameter:						
1.0–0.1 mm		28.9	24.2	26.0	4	80
0.1–0.02 mm		38.7	37.1	37.5	13	57
< 0.02 mm		32.4	28.4	30.5	7	73
< 0.002 mm		8.3	6.3	7.0	1	21
pH	in H_2O	6.63	7.14	7.36	5.50	7.91
	in KCl	5.22	6.21	6.55	3.88	7.07
$CaCO_3$ [g · kg^{-1} d.m.]		20.86	12.83	13.98	0.80	72.99
$C_{org.}$ [g · kg^{-1} d.m.]		19.7	17.6	19.4	1.2	54.0
Layer 10–30 cm						
Granulometric composition [%]: particle diameter:						
1.0–0.1 mm		24.6	20.9	22.0	5	52
0.1–0.02 mm		39.8	38.8	40.5	24	58
< 0.02 mm		35.6	32.8	33.5	13	68
< 0.002 mm		10.5	9.0	8.5	2	22
pH	in H_2O	6.68	7.34	7.65	5.54	8.10
	in KCl	5.33	6.30	6.65	4.21	7.07
$CaCO_3$ [g · kg^{-1} d.m.]		22.14	14.29	16.92	0.80	57.71
$C_{org.}$ [g · kg^{-1} d.m.]		11.3	9.3	11.2	0.5	19.6
Fresh alluvium						
Granulometric composition [%]: particle diameter:						
1.0–0.1 mm		45.4	36.1	44	2	98
0.1–0.02 mm		32.7	27.2	33	1	56
< 0.02 mm		21.9	16.5	20	1	67
< 0.002 mm		4.5	3.5	4	1	18
pH	in H_2O	7.47	7.53	7.51	7.09	8.21
	in KCl	7.17	7.25	7.24	6.66	7.99
$CaCO_3$ [g · kg^{-1} d.m.]		49.21	42.03	52.62	9.37	98.24
$C_{org.}$ [g · kg^{-1} d.m.]		18.4	14.0	19.0	0.42	79.8

Table 2 shows the total content of manganese and lithium and their forms soluble in 1 mole HCl · dm^{-3} in examined soils, fresh alluvium and plants.

The other figures relate to the minimum and maximum contents of manganese and lithium along with the corresponding quantile values 2.5 and 97.5. The quantiles give the image of the extreme values reduced by 5 % (the lowest and the highest values reduced by 2.5 % each).

Table 2

The contents of examined elements in alluvial soils, fresh alluvium and meadow grass of the San River Valley

Element	Layer	Arithmetic mean	Geometric mean	Median	Range	
					Minimum/ 2.5 quantile	Maximum/ 97.5 quantile
Total content in alluvial soils						
Mn	0–10 cm	617	584	575	256/285	1166/1040
	10–30 cm	611	580	564	261/263	1059/1053
Li	0–10 cm	25.38	24.05	24.40	9.5/11.3	44.2/20.4
	10–30 cm	25.38	24.29	24.55	12.8/12.9	41.7/38.2
Content of forms soluble in 1 mole HCl · dm^{-3} in alluvial soils						
Mn	0–10 cm	463	427	429	151/198	995/829
	10–30 cm	416	375	391	104/198	901/829
Li	0–10 cm	3.06	2.75	2.85	0.60/1.0	6.6/6.5
	10–30 cm	3.32	2.99	2.90	1.0/1.1	6.8/6.7
Total content in fresh alluvium						
Mn		753	624	554	270/297	3437/1818
Li		20.41	18.15	18.70	3.4/3.8	41.3/35.5
Content of forms soluble in 1 mole HCl · dm^{-3} in fresh alluvium						
Mn		637.24	514.55	450.00	188/195	2284/16.68
Li		1.94	1.69	1.90	0.2/0.3	5.1/4.9
Content in meadow grass						
Mn		58.31	46.82	43.50	16.8/17.9	228.8/219.2
Li		1.70	0.83	0.79	0.08/0.09	10.41/8.88

The occurrence of manganese is not only dependent on its concentration in the soil mother rock but also on soil forming processes which have the decisive influence on the distribution profile. The average content of manganese in various soil types ranged from 100 to 1300 mg · kg^{-1}. The results of the observations make it plain that sandy soils are poorer in manganese than clay soils and mineral soils have lower contents than organic ones [3]. Grass contains from 45 to 160 mg Mn · kg^{-1} d.m. on average, whereas clover from 25 to 85 mg Mn · kg^{-1} d.m. These figures are higher than the amounts suggested as sufficient in animal nutrition, which according to Falkowski et al [7] account for 10–20 mg · kg^{-1}. The concentrations of 400–2000 mg Mn · kg^{-1} in fodder plants may be harmful to animals [3].

Examined soils had the total manganese content in quite a wide range of values between 256–1166 mg · kg^{-1} d.m. No significant differences between the contents of analysed layers were found (see Table 2). The geometric mean of the total content amounted to 580 mg · kg^{-1} and was slightly higher in the turf layer. Manganese solubility (the share of the fraction soluble in 1 mole HCl · dm^{-3} in relation to the total content of manganese) in layer 0–10 cm was slightly higher than in layer 10–30 (see Table 3 for arithmetic mean 74.64 % and 67.73 %, respectively). The content of soluble forms in the sub turflayer was lower than in the turf layer.

The total contents of manganese in alluvium were higher than in the examined alluvial soils. The geometric mean amounted to 623.58 mg · kg^{-1} d.m., but there were also values which differed significantly from the geometric mean with the extreme result of 3437 mg · kg^{-1} d.m. which was almost threefold higher than maximum value determined in soils. It must be noted here that 97.5 quantile corresponded to 1818 mg · kg^{-1} d.m. The geometric mean of Mn soluble forms accounted for 514.55 mg · kg^{-1} d.m. and the range of variation was between 188 and 2284 mg · kg^{-1} d.m. in alluvium. Variations of manganese content in meadow grass of the examined San River Valley ranged from16.8 to 228.8 mg · kg^{-1} d.m. and the geometric mean was 46.82 mg Mn · kg^{-1} d.m.

Table 3

Solubility, ie, the share [%] of the fraction soluble in 1 mole HCl · dm^{-3} in relation to the total content of manganese and lithium

Element	Layer	Arithmetic mean	Geometric mean	Median	Range	
					Minimum	Maximum
Mn	0–10 cm	74.64	73.22	77.72	41.67	95.18
	10–30 cm	67.73	64.75	69.07	21.38	90.80
Li	0–10 cm	12.31	11.43	11.50	3.64	21.48
	10–30 cm	13.25	12.32	12.71	3.67	24.54
Mn	Fresh alluvium	83.04	82.52	84.03	65.51	99.54
Li		9.58	9.30	9.43	3.08	17.79

The alluvial soils of the studied parts of the San River Valley had relatively high concentrations of lithium ranging from 9.5 to 44.2 mg Li · kg^{-1} d.m., whereas the content of soluble fraction was 0.6–6.8 mg · kg^{-1} d.m. Alluvial soils were slightly richer in lithium than alluvium. The geometric mean of lithium contents in alluvium was 18.15 mg · kg^{-1} d.m. and variations ranged 3.4–41.3 mg · kg^{-1} d.m.

The geometric mean of the content of soluble lithium forms was 1.69 mg · kg^{-1} d.m. with variations between 0.2 to 5.1 mg · kg^{-1} d.m. The average solubility was slightly above 9 % and ranged from 3.08 to 17.79 %.

The geometric mean of lithium content in meadow green of the San River Valley amounted to 0.83 mg · kg^{-1} d.m. (see Table 2). The variations ranged from 0.08 to 10.41 mg · kg^{-1} d.m.

Discussion

The extent of manganese absorption in plants depends on its solubility. Solubility, on the other hand, is closely related to the soil reaction and becomes lower under acid conditions [3]. Kabata-Pendias and Pendias [3] provide a very wide range of the total contents of manganese in Poland's alluvial soils, ie from 150 to 1965 mg · kg^{-1} d.m. Similarly, great variations of the total content were noted in the examined fen soils of the San River Valley 256–1166 mg Mn · kg^{-1} d.m., and even much greater in fresh alluvium 270–3437 mg · kg^{-1} d.m. It must also be mentioned that the Mn content in 97.5 % alluvium samples was below 1818 mg · kg^{-1} d.m. What may come as a surprise is high Mn solubility connected with great concentrations of manganese soluble fraction in soils. The geometric mean of solubility in alluvial soils of the San River Valley was 68.86 % and in alluvium 82.52 % (see Table 3).

Grass usually contains 45–160 mg Mn · kg^{-1} d.m., which is more than the amounts needed in animal nutrition which according to Falkowski et al [7] range from 10 to 20 mg · kg^{-1}. The concentrations of 400–2000 mg · kg^{-1} in fodder plants may be harmful to animals [3]. The minimum Mn content in meadow grass is 10–20 mg · kg^{-1} d.m. as reported by Falkowski et al. However, Borowiec and Urban [8] claim that these contents may be much higher, ranging from 50 to 100 mg · kg^{-1} d.m.

According to Kabata-Pendias and Pendias [3] the total lithium content in Poland's soils varies between 0.01 and 40 mg · kg^{-1} d.m. The content of lithium in alluvial soils of the San River Valey ranged similarly, while slightly lower values were determined in fresh alluvium.

Meadow grass of the San River Valley was enormously diverse as it comes to lithium concentrations but the geometric mean was only 0.83 mg · kg^{-1} d.m. Following the assumption made by Falkowski et al [7] that meadow grass rich in valuable chemical components should contain minimum 1 mg Li · kg^{-1} d.m., it must be said that most samples had lithium content approximating the minimum value. Positive correlation between the lithium content in meadow grass and the content of forms soluble in 1 mole HCl · dm^{-3} in soils was found [9].

The alluvial process enriches riparian areas of the San River Valley with biogenic elements, including manganese and lithium. Extensive research revealed no contamination of the grasslands by these elements. It must be emphasized that alluvial terrains provide flood protection as they trap excess water and cause its flow to slow down. Proper management of alluvial terrains will make it possible to take full advantage of fresh alluvium as a natural fertiliser.

Conclusions

1. Due to their very dynamic character, alluvial processes cause variations of biogenic elements distribution in soil and play an important role in determining floral compositions and diversity of the ground vegetation.

2. Fresh alluvium deposited by floods in the San River Valley is rich in manganese and lithium but these contents do not differ greatly from the typical concentrations of soils.

3. High Mn solubility in the alluvium has been observed despite the neutral reaction of the alluvium. Manganese is therefore more available to plants. Highly soluble

manganese was not easily absorbed by meadow grass which might be explained by the neutral and even acid reaction of the soil in this environment.

4. The manganese content in meadow grass of the San River Valley proved sufficient for dietary intake, whereas a small deficiency of lithium in some samples were observed.

5. It is required that riparian areas be carefully protected due to their ecological value, agricultural function and flood protection they provide.

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ODDZIAŁYWANIE PROCESU NAMULANIA NA OBIEG MANGANU I LITU W ŚRODOWISKU ŁĘGOWYM

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Abstrakt: Lit i mangan są mikroelementami niezbędnymi do prawidłowego funkcjonowania organizmów roślinnych, zwierzęcych, jak i samego człowieka. Mimo to, są to pierwiastki, które występując w nadmiarze, mają działanie toksyczne. Badania przeprowadzono na terenach łąk łęgowych w dolinie rzeki San. Badano określone elementy obiegu pierwiastków w środowisku, obejmującym gleby aluwialne, świeże namuły odmładzające profile glebowe oraz roślinność łąk łęgowych.

Przeprowadzone badania potwierdzają ważną rolę procesu namulania w obiegu litu i manganu w środowisku łęgowym. Proces ten może być brany pod uwagę jako jeden z elementów bilansu tych pierwiastków oraz kształtowania ich dostępności dla roślin.

Słowa kluczowe: gleby aluwialne, świeże namuły, metale ciężkie, mangan, lit

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PROPERTIES OF SOILS SURROUNDED TRZUSKAWICA LIME PLANT INDUSTRY S.A., DEPARTMENT OF KUJAWY

WŁAŚCIWOŚCI GLEB W OTOCZENIU ZAKŁADÓW PRZEMYSŁU WAPIENNICZEGO TRZUSKAWICA S.A., ZAKŁAD KUJAWY

Abstrakt: Effect of pollutants emitted by plants Trzuskawica Lime Industry S.A., Department of Kujawy and Lafarge "Cement" on the physicochemical properties of soils in this region, mainly pH and the state of exchangeable complex was studied.

Soil samples were collected in late August and September 2007, during post-harvest. There were 16 soil samples selected from arable-humus horizon, from the area of about 4000 m^2. In the samples taken for analysis active and exchangeable acidity, hydrolytic acidity, calcium carbonate, total exchangeable cations, and organic C content were determined. Statistical analysis was performed using STATISTICA 8.0 PL programme.

As a result of the studies there were found a high degree of soils alkalization, due to high accumulation of lime pollutants emitted in the past, and high natural content of calcium carbonate in soils in the vincinity of plants. The highest share of Ca^{2+} ions in the cation exchangeable capacity of soil complex there was found. The degree of cation saturation of analyzed soils and their cation exchange capacity was significantly related to the content of alkaline cations. Comparison of results from the years 1992–2007 indicates a continuing high pH values and the nature of saturation of soil exchangeable complex due to the presence of exchangeable calcium in the soils surrounding Trzuskawica Lime Plant Industry S.A., Department of Kujawy and Lafarge "Cement".

Based on the studies can not be determine the impact of each individual, the two largest plants, emitting limestone pollutants, on the environment in their surroundings.

Keywords: dusts, exchangeable complex, lime, soil

Anthropogenic emissions of various compounds into the atmosphere are one of the factors causing its pollution. It should be highlighted that the most emerging contaminants enters the environment mainly through the atmosphere, which makes it

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possible to spread them over considerable distances, and point sources of pollution takes the territorial nature. Atmospheric pollutions also cause changes in the soil environment. As a result of human activities the atmosphere is entered by hundreds of thousands of different pollutants. These include carbon, sulfur and nitrogen oxides and also dusts, which formation is associated with all production and combustion processes [1].

Cement and lime industry, considered the most dust-producing, constitutes a major part in the contamination of soils. Emission occurs at each stage of production from extraction by crushing the raw material to transport [2]. Literature reports about the danger of dusts and gas pollutions, which cause lowered yields of crops in the vincinity of the cement plants [3].

The aim of this study was to assess the impact of pollutants emitted by Trzuskawica S.A. Lime Plant Industry, Department of Kujawy and Lafarge "Cement" on the physicochemical properties of soils in surrounding area. The comparison of results from years 1992–2007 was also made [4].

Material and methods

As a research material 16 soil samples from arable-humus horizon of an area surrounded by Trzuskawica Lime Plant Industry S.A., Department of Kujawy, were collected. Sampling sites corresponded to the location of soil sampling in 1992 for the impact assessment of KCW Kujawy on soil pH [4].

In dried and sieved (with a 1 mm diameter mesh sieve) samples the following physicochemical soil properties were determined: pH in H_2O and in 1 mol $\cdot$ dm^{-3} KCl solution, hydrolytic acidity (Hh) using Kappen's method, the total content of organic carbon using Turin's method, the content of $CaCO_3$ by Scheibler and the content of exchangeable bases were determined by Pallmann, the contents of Ca^{2+}, K^+ and Na^+ were determined by emission and Mg^{2+} by absorption atomic spectrometry, using a PU 9100X Philips spectrometer.

The statistical analysis of the results was evaluated with STATISTICA 8.0 PL computer programme.

Results and discussion

The properties of soils are presented in Tables 1 and 2. Emission of dusts is an important factor affecting the natural environment. Often, the effects of the impact of dust on plants can be manifested through changes in the properties of soil [5]. Compared the active acidity with the results obtained in 1992 it was reported a slight decrease of pH value, only one sample (No. 13) had the same value, and samples 5 and 15 showed an increase of pH. Similar results were obtained in the case of exchangeable acidity: samples 2, 13, 15 and 16 had similar value, samples 5 and 6 showed a slight increase, and the remaining samples had a slightly lower pH than in 1992. Such a high soil pH can be closely linked with the presence of dust in the studied area [2]. Changes in soil pH, observed in previous studies, are accompanied by far-reaching changes in the exchangeable complex.

Table 1

Physical and chemical properties of soil (1992)

No.	$CaCO_3$	$C_{org.}$	Acidity			Exchangeable cations				TEB	CEC	Base saturation [%]
			pH		Hh	Ca	Mg	K	Na			
	[g · kg^{-1}]		H_2O	KCl	[mmol · kg^{-1}]							
1	15.3	7.0	7.97	7.92	0.2	122.4	4.1	4.4	1.3	132.2	132.4	99.9
2	n.d*	6.0	7.93	7.56	1.2	48.0	2.3	1.4	1.0	52.7	53.9	97.8
3	n.d.	6.2	7.61	7.40	2.2	47.3	2.3	1.7	1.5	52.8	55.0	96.0
4	n.d.	7.0	7.34	7.03	4.1	40.4	2.5	1.8	0.9	45.6	49.7	91.8
5	n.d.	9.4	6.94	6.28	10.2	33.4	3.3	2.0	1.0	39.7	49.9	79.6
6	9.8	6.8	7.99	6.85	0.9	121.1	3.5	1.0	0.9	126.5	127.4	99.3
7	11.0	8.6	7.84	7.64	0.8	119.3	3.7	2.9	1.1	127.0	127.8	99.4
8	4.2	5.8	8.03	7.57	1.1	109.1	3.9	4.1	1.1	118.2	119.3	99.1
9	13.6	7.3	8.19	7.79	1.3	108.8	3.3	2.4	0.8	115.3	116.6	98.9
10	14.8	5.2	8.19	7.93	1.2	95.0	3.0	1.5	0.8	100.3	101.5	98.8
11	n.d.	5.8	7.73	7.54	2.3	59.2	2.8	0.8	1.0	63.8	66.1	96.5
12	22.1	9.6	7.50	7.39	2.6	117.2	4.4	3.5	1.3	126.4	129.0	98.0
13	2.5	7.7	7.56	7.50	2.1	61.3	2.4	4.8	0.9	69.4	71.5	97.1
14	n.d.	7.6	7.12	6.93	3.7	48.0	2.5	3.5	2.2	56.2	59.9	93.8
15	n.d.	9.1	6.23	6.06	12.4	36.3	4.9	2.2	2.2	45.6	58.0	78.6
16	1.7	6.7	7.53	7.28	2.1	48.8	1.7	3.5	2.3	56.3	58.4	96.4

* – not detected.

Table 2

Physical and chemical properties of soil (2007)

No.	$CaCO_3$	$C_{org.}$	Acidity			Exchangeable cations				TEB	CEC	Base saturation [%]
			pH		Hh	Ca	Mg	K	Na			
	[$g \cdot kg^{-1}$]		H_2O	KCl	[$mmol \cdot kg^{-1}$]							
1	67.9	2.7	7.61	7.53	2.0	100.9	2.5	8.1	1.1	112.6	114.6	98.3
2	22.9	1.9	7.58	7.51	2.1	96.5	1.4	2.7	0.2	100.9	103.0	98.0
3	11.9	4.4	7.26	7.16	2.5	52.1	2.5	3.2	0.2	58.0	60.5	95.9
4	n.d.*	1.5	6.63	6.50	8.3	35.9	1.5	1.0	0.1	38.5	46.8	82.3
5	57.3	1.5	7.48	7.42	1.9	116.2	4.7	2.5	0.3	123.7	125.6	98.5
6	20.4	2.7	7.62	7.45	2.0	98.7	2.0	3.0	0.2	103.9	105.9	98.1
7	21.2	4.0	7.47	7.35	2.2	96.2	1.4	3.4	0.2	101.2	103.4	97.9
8	18.7	5.2	7.36	7.27	2.4	94.4	2.2	6.9	0.2	103.7	106.1	97.7
9	40.3	2.0	7.48	7.44	2.2	96.6	2.9	3.3	0.1	102.8	105.0	97.9
10	12.7	1.5	7.24	7.20	2.9	68.4	1.5	2.5	0.2	72.6	75.5	96.2
11	18.7	1.9	7.50	7.42	1.8	107.3	1.5	3.4	0.1	112.3	114.1	98.4
12	13.6	2.3	7.28	7.24	2.4	81.3	1.2	5.1	0.2	87.8	90.2	97.3
13	40.3	4.2	7.57	7.49	2.1	100.5	1.6	3.4	0.2	105.7	107.8	98.1
14	12.7	0.3	7.38	7.20	2.2	69.5	1.5	3.5	0.2	74.6	76.8	97.1
15	n.d.	3.9	6.56	6.12	9.8	61.2	3.6	5.6	0.4	70.8	80.6	87.8
16	36.1	3.0	7.33	7.21	2.3	86.0	3.2	4.7	0.2	94.1	96.4	97.6

* – not detected.

Determination of hydrolytic acidity is needed mainly to precise needs of soil liming. Both in 1992 and 2007 the value of Hh was very low. In 1992, ranged between 0.2 and 12.4 mmol · kg^{-1}, and in 2007 from 1.8 to 9.8 mmol · kg^{-1}, no significant differences were noticed.

The percentage base saturation during the analyzed period ranged from 82.3 to 98.5 %. Statistical analysis showed almost complete negative correlation ($r = -0.937$) between the hydrolytic acidity and the degree of cation saturation of exchangeable complex.

From this researches follows that, apart from minor fluctuations, the sum of alkaline cations remains unchanged in studied years. Our results showed small reduction of cation exchangeable capacity in relation to the year 1992.

High share of Ca^{2+} in the soil exchangeable cations of soil complex is reflected in the degree of soil base saturation. This observation was confirmed in the statistical analysis which showed very high value of correlation coefficient amounting 0.787 between these variables. Accordingly, a significant correlation between the hydrolytic acidity and Ca^{2+} content was also registered. In this case the correlation coefficient was negative and is equal –0.680.

Exchangeable cations in the soil exchangeable complex should be present in appropriate proportions. According to different authors, the average percentage of each cation should be 65 % of Ca, 10 % Mg, 5 % K and 20 % H, which gives the ratio of Ca:Mg:K:H equals 14:2:1:4 [8, 9]. In the studied soil samples Nos. 3, 12 and 16 the content of K^{+} and in soil sample No. 4 the content of H^{+} are very similar to the contents of the most common. In other soil samples, these values deviate far from the standards.

Almost all samples showed an increase of $CaCO_3$ content in relation to 1992. It is a component of anthropogenic origin and may come from the alkaline dusts emitted by plants [6, 7]. Significant emissions from fugitive sources of dusts, method of extraction and transport of raw material could be a reason of such situation. With the increase of calcium carbonate content hydrolytic acidity decreased, as was indicated by high correlation coefficient ($r = -0.546$), and simultaneously the degree of base saturation inreased ($r = 0.568$).

Registered organic carbon content was significantly lower than in 1992. Impact on such a low value could be the fact that the samples were collected during post-harvest. Reduction of humus content can also be caused by limited use of manure in the study area. It is also known that under alkaline conditions follows a rapid mineralization of humus.

Conclusions

1. In connection with the structural changes of the Cement and Lime Plant into two separate companies, ZPW Trzuskawica S.A., Department of Kujawy and "Lafarge" Cement, it is difficult to assess the impact of each of them separately on the state of the soil environment.

2. In 2007 compared with 1992 the decrease in organic carbon content in the studied soils was observed. This is due probably to the limited organic fertilization of soils and accelerated mineralization of humus under alkaline conditions.

3. Based on the study there was found a high degree of alkaline soils due to high accumulation of pollutants emitted from limestone in the past. The results of studies from year 1992 and 2007 indicate that there are still high pH values, and soil exchangeable complex is largely saturated by exchangeable forms of calcium.

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WŁAŚCIWOŚCI GLEB W OTOCZENIU ZAKŁADÓW PRZEMYSŁU WAPIENNICZEGO TRZUSKAWICA S.A., ZAKŁAD KUJAWY

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Abstrakt: Przedmiotem badań był wpływ zanieczyszczeń emitowanych przez Zakłady Przemysłu Wapienniczego Trzuskawica S.A., Zakład Kujawy i Lafarge „Cement”, na fizykochemiczne właściwości gleb uprawnych w tym rejonie, przede wszystkim odczyn i stan kompleksu sorpcyjnego.

Próbki gleb do badań zostały pobrane na przełomie sierpnia i września 2007 r., w okresie pożniwnym. Do badań wytypowano 16 próbek glebowych z poziomu ornopróchnicznego, z obszaru o powierzchni około 4000 m^2. W pobranych do analizy próbkach oznaczono kwasowość czynną i wymienną, kwasowość hydrolityczną oraz zawartość węglanu wapnia, zasadowych kationów wymiennych i C-organicznego. Obliczenia statystyczne wykonano z wykorzystaniem programu komputerowego STATISTICA 8.0 PL.

Na podstawie przeprowadzonych badań stwierdzono wysoki stopień alkalizacji gleb, wynikający z dużej akumulacji zanieczyszczeń wapiennych emitowanych w przeszłości oraz dużej naturalnej zawartości węglanu wapnia w glebach w otoczeniu zakładów. Największy udział w kationowej pojemności wymiennej kompleksu sorpcyjnego miały jony Ca^{2+}. Stopień wysycenia analizowanych gleb zasadami oraz ich pojemność sorpcyjna były istotnie związane z zawartością kationów o charakterze zasadowym. Porównanie wyników badań z lat 1992–2007 wskazuje na utrzymujące się duże wartości pH i stopnia wysycenia zasadami glebowego kompleksu sorpcyjnego, spowodowany obecnością wymiennych form wapnia w glebach w otoczeniu Zakładów Przemysłu Wapienniczego Trzuskawica S.A., Zakład Kujawy i Lafarge „Cement”.

Na podstawie przeprowadzonych badań nie można określić wpływu każdego z osobna, dwóch największych zakładów, emitujących zanieczyszczenia wapienne, na stan gleby w ich otoczeniu.

Słowa kluczowe: pyły wapienne, kompleks sorpcyjny, gleba

E C O L O G I C A L C H E M I S T R Y A N D E N G I N E E R I N G A

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OCCURRENCE OF SOME HEAVY METALS IN BOTTOM SEDIMENTS OF LOBELIA LAKES

WYSTĘPOWANIE WYBRANYCH METALI CIĘŻKICH W OSADACH DENNYCH JEZIOR LOBELIOWYCH

Abstract: The paper presents the occurrence of zinc (Zn), copper (Cu) and manganese (Mn) in bottom sediments of selected Lobelia lakes which are specific and unique aquatic reservoirs. The lake sediments were sampled in summer stagnation in the surface layer at two stands in each lake: in littoral zone and in profundal zone at maximum depth of the lake.

Results of the investigations show that Zn, Cu and Mn contents in the investigated bottom sediments were low and ranged within geochemical background limits or slightly exceeded them. Presence of the metals in the sediments was spatially differential. Zn, Cu and Mn contents were significantly higher in most cases in the profundal zone of each investigated lake than they were in the litoral zone. Another factor which significantly differs the heavy metals content was level of thermal stratification.

Keywords: heavy metals, bottom sediments, Lobelia lakes

Bottom sediments are an important element of water ecosystems useful for control of quality of the environment. Bottom sediments are produced as a result of sedimentation of mineral and organic matter coming from erosion and the elements precipitated from water. Bottom sediments are also produced by the material carried with industrial and municipal sewage into surface waters.

Production and properties of lake bottom sediments depend on a number of factors including geological structure, character and use of the basin, thermal conditions and mixing of the lake waters as well as oxygenation or vegetation type etc. [1].

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Bottom sediments are irreplaceable archives, which reflect climate and environmental change being the same a valuable source of paleo-environmental information. Bottom sediments are a kind of trap for quite a lot of material carried into the lake. Lake sediments accumulate most potentially hazardous heavy metals and other organic compounds [2]. The heavy metals content may be a substantial indicator and a source of information on the impact of anthropopresion on the water environment [3, 4].

Heavy metals in sediments have attracted much attention recently because of their toxic nature [5]. They are brought in the environment as a result of natural processes occurring in the nature as well as a result of agriculture and industrial activity. Heavy metals are deposited in bottom sediments where they are temporarily immobilized and in this way they may be a source of secondary pollution. In favourable conditions the heavy metals may be released from the bottom into water but this process depends on the form in which given metal occurs in the sediments, as well as pH and redox conditions of the environment [6, 7].

This paper is an initial stage of research related to the overall assessment of sediment quality in Lobelia lakes for contamination by heavy metals. Lobelia lakes are specific and unique aquatic reservoirs on a global scale.

The main aim of this work is to determine the total content and stowage of heavy metals such as zinc (Zn), copper (Cu) and manganese (Mn) in bottom sediments from selected Lobelia lakes.

Material and methods

The material of this study was samples of bottom sediments from the chosen Lobelia lakes. In EU Lobelia lakes are declared to be endangered ecosystems of European importance. In Poland there are about 170 Lobelia lakes, mainly situated on the West Pomeranian Region. There are four lakes, namely Jelonek, Morskie Oko, Wielkie Oczko and Ciemino selected for investigations (as shown in Fig. 1). These lakes differ in morphometric structure, use of basin, trophy and thermal conditions of waters.

The Jelonek Lake is a small aquatic reservoir surrounded by poor sandy fields – arable land is only 78 %. The lake belongs to aquatic reservoirs of dystrophic type. In summertime it has deficient thermal stratification. There is abundant vegetation characteristic for lobelia lakes.

The Morskie Oko Lake is a small round aquatic reservoir. It is deep and it has full thermal stratification. It is surrounded by mixes coniferous forests. Kraska [8] classifies the lake as well-balanced lake. The lake is plentiful of species typical for lobelia lakes. The lake is recommended for strict protection.

The Wielkie Oczko Lake is a small round quite shallow aquatic reservoir. It is surrounded by forest mainly pinewood with some of Pomeranian beech. There is occasional *Lobelia dortmanna* and plentiful *Myriophyllum alterniflorum.* In summertime the lake has not got full thermal stratification. It is a balanced lake in danger. It is also recommended for protection.

The Ciemino Lake is a big and deep aquatic reservoir. It has very diversified shoreline. In summer stagnation it has full thermal stratification. A basin of the lake in

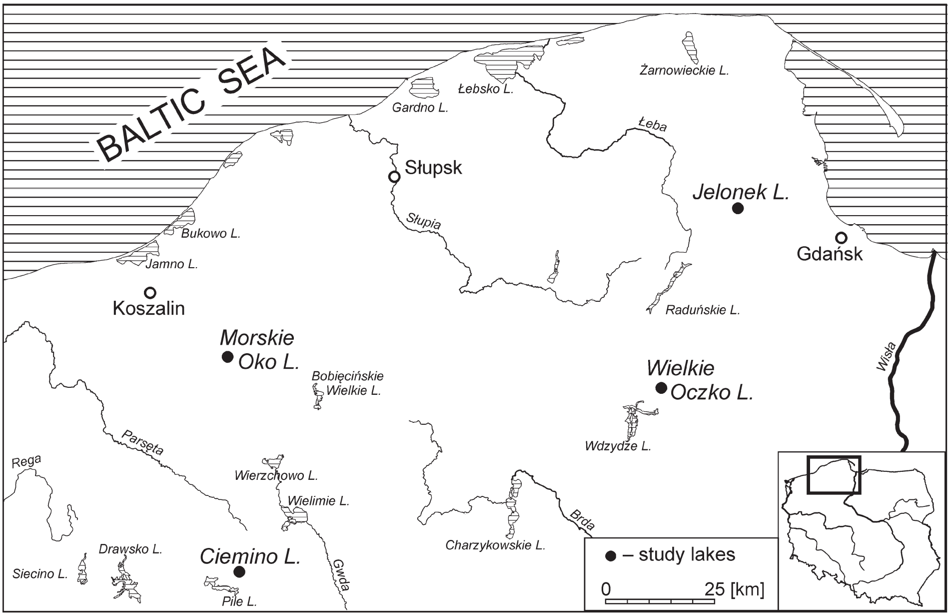

Fig. 1. Map showing location the studied lakes

50 % consists of forests, mainly deciduous ones with Pomeranian beech. The lake belongs to eutrophic reservoirs. Observed degradation of the lake is caused by village buildings situated in the immediate vicinity of the lake, slurry coming into the lake and liming which is an element of fishing farming. In the lake there is occasional *Myriophyllum alterniflorum*.

All of the studied lakes are not-flow reservoirs. In Table 1 are presented the selected morphometric and hydrochemical parameters of the lakes.

Table 1

The selected morphometric and hydrological parameters of the studied lakes

Parameter	Jelonek	Wielkie Oczko	Morskie Oko	Ciemino
Longitude	54°26.8′	54°03′30″	54°04′30″	53°38′
Latitude	18°15′	18°00′20″	16°28′40″	16°34′
Maximum depth [m]	3.5	10.0	19.2	13.4
Area [ha]*	9.0	3.6	4.9	241.7
pH	5.8	7.6	7.1	8.1
Secchi disc visibility [m]	3.5	3.0	5.6	2.8
Thermal stratification	incomplet	incomplet	full	full
Use of catchment	72 % of arable land	100 % pine forests and acid beech Pomeranian	100 % mixed forests	52 % deciduous forests and acid beech Pomeranian

* Area lakes by Choinski [9].

The water and sediments were sampled in summer stagnation. The samples of sediments were taken in the surface layer up to 20 cm with the aid of Kajak's device. The randomly chosen 4–6 samples taken at one sampling stand were mixed and they were treated as a cumulative sample. Bottom sediments were sampled at two stands in each lake:

– in the coastal zone (samples A),

– in profundal zone at maximum depth of the lake (samples B).

In dried and crushed samples were examined organic carbon ($C_{org.}$), Cu, Zn and Mn. Organic carbon content was determined with Orlov and Grindel method [10]. The heavy metals were determined by *atomic absorption spectrophotometer* (AAS), after previous mineralization of samples in *aqua regia* [11].

Statistical analysis was performed in order to verify the significance of differences between the analyzed parameters. Tukey's test was performed. Also the Pearson correlation coefficient was applied in order to determine the significance of relationships between Cu, Zn, Mn and C_{org}.

Results and discussion

The analytical results are summarized in Table 2.

Table 2

Organic carbon and selected heavy metals contents

Lake	Zone	$C_{org.}$ [%]	Cu	Zn	Mn
			[mg · kg^{-1}]		
Lake of the incomplete thermal stratification of water					
Jelonek	A*	21.0^{c}	7.9^{c}	92.3^{d}	105.3^{d}
	B	21.1^{c}	8.9^{d}	108.3^{e}	89.4^{c}
Wielkie Oczko	A	20.8^{c}	6.9^{b}	67.7^{c}	261.5^{g}
	B	20.3^{c}	10.9^{e}	92.4^{d}	165.3^{f}
Lake of the full thermal stratification of water					
Morskie Oko	A	0.4^{a}	0.4^{a}	2.3^{a}	5.1^{a}
	B	29.5^{d}	19.3^{g}	150.5^{g}	124.8^{e}
Ciemino	A	0.7^{a}	1.01^{a}	12.5^{b}	31.6^{b}
	B	13.0^{b}	11.9^{f}	138.3^{f}	428.7^{h}

*A – samples of sediments from litoral zone; B – samples of sediments from profundal zone; means marked by the same letters did not differ significantly at $p < 0.05$.

Results obtained in the analysis of bottom sediments sampled in the investigated lakes show that the sediments may be described as not polluted with zinc, copper and manganese as in most reservoirs content of these metals corresponds to a level of geochemical background or only slightly exceeds the level [12].

It was observed significant differences in content of the investigated metals between the studied lakes. These differences arise from, *inter alia* trophy character of the reservoirs, and the use of their basins. The factors, which determine setting of the investigated metals in bottom sediments the most strongly is the place of deposit sediments in the lake basin and level of thermal stratification.

In the bottom sediments deposited at the maximum depth of the lake concentration of Cu and Zn was significantly statistically higher than it was in the bottom sediments deposited in the litoral zone. In the bottom sediments in a profundal zone Zn and Cu content reaches higher values than the range of geochemical background. The overall elevated concentrations of the elements at these lakes may be attributed to multiple factors. Both Zn and Cu may be introduced into the lakes with surface wash and municipal sewage. In particular, this situation may occur in lakes Ciemino and Jelonek. On the other hand, the source of elevated concentration of Cu and Zn can be precipitation.

However, values of Cu and Zn are close to the limit between the geochemical background and the I class and should not constitute a greater threat to the purity of the studied lakes.

Another factor which significantly differs Cu and Zn content is level of thermal stratification. In bottom sediments of the lakes (Jelonek Lake and Wielkie Oczko Lake) where the thermal stratification is not full, Zn and Cu content is almost the same in both the litoral zone.

The lakes Jelonek and Wielkie Oczko are shallow reservoirs. These lakes operate differently than deep lakes [13], due to the different dynamics of water masses, and therefore other circulation of matter. Evenly arrangement of Cu and Zn in sediments of these lakes may be due to resedimentation induced on resuspension or the result of bioturbation [14].

Furthermore in the lakes in which during summer stagnation there is not hypolimnion that is a kind of a trap for different types of pollution including heavy metals, the metals are not cumulated in the bottom sediments but they may be released and they include in the circulation in the whole aquatic reservoir.

In the lakes with full thermal stratification Zn and Cu content in the litoral zone waters is below the range of geochemical background and in profundal zone waters the content exceeds the range of geochemical background. Enrichment of profundal sediments with heavy metals may be caused by less intensive water mixing and water erosion due to which some sediments are carried on the slope of a lake basin from shallow parts of the lake towards the deeper layers [14, 15].

Due to the large number of factors influencing the processes of depositing sediment in lakes, only a broader survey will answer what causes the different distribution of metals in the sediments of lakes.

The milder hydrochemical processes in the deepest parts of a lake, especially that where the thermal stratification is full, cause that deposited in the profundal zone sediments contain more organic matter which is reflected in organic carbon content. In analysed sediments Zn and Cu content significantly correlates with organic C content (Cu: $r = 0.93$, Zn: $r = 0.87$). High contents of Zn and Cu are recorded in samples with high content of organic matter. Similar relations were obtained also by other researchers

[16–19]. It confirms the important role of organic matter in distribution processes of heavy metals in the aquatic system [20, 21].

Manganese content in bottom sediments is also diversified and the factor of high importance is here water mixing and the place of setting of the metal in the lake basin. However, tendency of changes is unlike Cu and Zn. There is observed characteristic tendency of changes in concentration of manganese in connection with different mixing of a lake. In bottom sediments of lakes with full thermal stratification small contents of manganese occur in the litoral zone and its concentration instantly increases in the profundal zone. In profundal sediments of the Ciemino Lake where degradation of the reservoir is noticeable Mn content reaches maximum value of 428.7 $\mathrm{mg} \cdot \mathrm{kg}^{-1}$ dry matter. In bottom sediments without full thermal stratification tendency of the changes in Mn content is reverse. In the litoral zone Mn content is higher than in sediments deposited in profundal zone. Full mixing of the lake waters in autumn and spring circulation allows the mineral substances to be distributed in the whole lake and it leads to saturation of all water layers with oxygen coming from the air. That may affect the changes in chemical properties of polyvalent elements like manganese.

There was non-significant correlation between C_{org} content and the Mn content in the sediments of studied lakes (Table 3).

Table 3

The Pearson correlation matrix for organic carbon and heavy metals

Parameter	$C_{org.}$	Cu	Zn
Cu	0.95*	—	
Zn	0.82*	0.94*	—
Mn	0.30	0.45	0.59

* Correlation coefficient is significant at the 0.05 level.

Similar poor associations of Mn with other trace metals in sediments were also noticed by Alagarsamy [19] for Mandovi estuary, west coast of India and by Chatterjee et al [20] for the lower stretch of Hugli (Ganges) estuary, northeast coast of Bay of Bengal.

Conclusions

Results of the investigations show that Zn, Cu and Mn contents in bottom sediments in the investigated were low and ranged within geochemical background limits or slightly exceeded them.

Presence of the metals in the sediments was spatially differential. The spatial distributions of trace elements in lakes sediments are influenced by so many factors and hence it is difficult to find the principal one. But to a large extent the observed differences in the contents of Zn, Cu and Mn are associated with different conditions of sedimentation in a given zone of a lake as well as with different content of organic matter, which plays an important role in depositing of the metals in bottom sediments.

Moreover, the observed spatial distribution of heavy metals is related to the basin's nature, appears to play a great importance for the observed differences.

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WYSTĘPOWANIE WYBRANYCH METALI CIĘŻKICH W OSADACH DENNYCH JEZIOR LOBELIOWYCH

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Abstrakt: W pracy przedstawiono występowanie cynku, miedzi i manganu w osadach dennych wybranych jezior lobeliowych, stanowiących specyficzną grupę jezior. Osady jezior pobierano w okresie stagnacji letniej z warstwy powierzchniowej, z dwóch miejsc: strefy brzegowej i w miejscu maksymalnej głębokości zbiornika.

Wyniki badań zawartości cynku, miedzi i manganu w osadach badanych jezior wskazują, że stężenia tych pierwiastków były niskie i mieściły się w granicach tła geochemicznego lub nieznacznie je przekraczały. Obecność analizowanych metali w osadach była zróżnicowana przestrzennie. W większości przypadków zawartość cynku, miedzi i manganu była istotnie większa w osadach deponowanych w miejscu maksymalnej głębokości każdego jeziora w porównaniu z zawartością tych metali w osadach strefy litoralu. Czynnikiem, który istotnie różnicował zawartość analizowanych metali, była wykształcona w pełni stratyfikacja termiczna wód lub jej brak.

Słowa kluczowe: metale ciężkie, osady denne, jeziora lobeliowe

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SORPTION OF THE SURFACTANT HYAMINE 1622 IN SOILS

SORPCJA SURFAKTANTU HIAMINY 1622 W GLEBACH

Abstract: A study was performed on the sorption of hyamine 1622, a cationic surfactant, from water solutions in 3 soils which, with relation to the character of their parent rocks, are referred to in this paper as a sandy soil, a loess soil and a loamy soil, respectively. The sorption process was executed with the static method: 2-gram weighed portions of soil were placed in polyethylene test tubes, adding 10 cm^3 of solution with hyamine concentration in the range from 0.00015 to 0.006 $mol \cdot dm^{-3}$, and then shaken for 6 hours. The level of sorption of hyamine was determined with relation to the concentration and pH of the initial solution, to the time of soil-solution contact, and in the presence of electrolytes KCl and KNO_3 in the surfactant-electrolyte systems = 1 : 1 and 1 : 10.

The experiments showed that with increase in the concentration of the initial solution there was an increase of hyamine sorption in the soils. It was established that the affinity sequence of the studied soils with relation to hyamine was as follows: loamy soil > loess soil > sandy soil. With increase in the pH value only slight changes were observed in the sorption effectiveness in the sandy and loess soils, while in the loamy soil the sorption remained at a constant level. Kinetic tests revealed that in the sandy and loess soils the sorption proceeded the fastest during the initial 15 minutes, and extension of the time of the soil-solution contact to 720 minutes did not produce any notable changes in the level of the sorption. In the loamy soil hyamine sorption at the level of 100 % was observed irrespective of the time of contact of the solution with the soil. The sorption process proceeded in accordance with the mechanism of pseudo second-order reaction. The presence of electrolyte caused both a reduction and an increase in the sorption of hyamine in the sandy and loess soils, but the extent of the changes was related to the type of electrolyte and to the concentration of the surfactant. Electrolyte addition had no effect on hyamine sorption in the loamy soil.

Keywords: cationic surfactant, sorption, soil

Surfactants are compounds with asymmetric structure, composed on a non-polar “tail” which is frequently a long hydrocarbon chain, and a polar “head” which has an ionic or a dipole character [1]. The compounds are commonly used as components of detergents and emulsifiers. Certain surfactants are also used for the removal of organic contaminants and heavy metals from soils. Currently an increase is observed in the level of environmental pollution with those compounds, resulting from intensive economic

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growth. Surfactants penetrate into the environment with industrial and domestic sewage and with wastes of various kinds [2, 3].

Cationic surfactants are characterised by having a polar "head" with a positive charge, eg quaternary ammonium salts [4]. They are substances that have a toxic effect on soil microorganisms and an unfavourable effect on the physicochemical properties of soils. Sorption plays an important role in the fate of surfactants in soils. According to Lee et al [5], the sorption of surfactants is strongly influenced by the properties of soils, such as: organic matter content, clay content, electrolyte content and pH, as well as the molecular structure of the surfactant. In the opinion of Muherei and Junin [6], in water solution, the surfactant exist as monomers at low concentration. When surfactant concentration is above a critical value termed the *critical micelle concentration* (CMC), the surfactant molecules aggregate and form micelles. At concentrations above the CMC, the sorption of the surfactant reaches a plateau.

Hyamine is quaternary ammonium salts of cationic surfactant character [1]. Due to the antibacterial and antifungal properties this compound is used in households and in medical consulting rooms and dentists' surgeries. After use, hyamine with the wastewater goes to the various components of the environment, including the soil, which is subject to sorption. Knowledge of the sorption is essential to estimate the bioavailability of hyamine and may be used in studies of the degradation of the surfactant. But one article [1] in the literature, there is no information about the sorption of hyamine in soils. Therefore, there is a need for experiments that would provide an explanation of the behaviour of hyamine in soils.

The objective of the study presented here was examination of the process of sorption of a cationic surfactant, hyamine 1622, in three soils with differing properties, with relation to the concentration of the surfactant, duration of the sorption process, pH of the solution, and an addition of electrolytes.

Material and methods

For the sorption experiments three soils were used, the following types of: a grey-brown podzolic soil developed from sand with the particle size distribution of loamy sand, a grey-brown podzolic soil developed from loess, with particle size distribution of silt, and a brown soil developed from boulder loam, with the particle size distribution of sandy clay loam (soil types according to the classification of the Polish Soil Science Society from 1989 [7]; particle size distribution according to the classification of the Polish Soil Science Society from 2008 [8]), further referred to in the paper, due to the character of their parent rocks, a sandy soil, a loess soil and a loamy soil. Samples of the soils were taken from the A_p horizon, air dried, then screened through a sieve with 2 mm mesh, and averaged. The physicochemical properties of soils are given in Table 1.

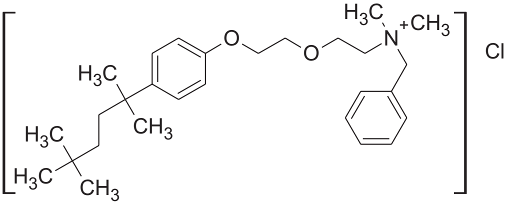
Grain size composition was determined with the Cassagrande method as modified by Proszynski, organic carbon content with the method of Tiurin, pH in $1 \text{ mol} \cdot \text{dm}^{-3}$ KCl – electrometrically, specific surface area with the method of water vapour adsorption, hydrolytic acidity (H_h) acc. to procedure PB-38 and sum of exchangeable cations (S) acc. to procedure PN-R-04027:1997 and sorptive capacity (T) as sum H_h and S.

Table 1

Physicochemical properties of soils

Soil	Share of soil fraction [%] with diameter [mm]				pH in 1 mol · dm^{-3} KCl	Organic carbon content [g · kg^{-1}]	Specific surface area [m^2 · g^{-1}]	Hydrolytic acidity (H_h) [mmol H$^+$ · kg^{-1}]	Sum of exchangeable bases (S)	Sorptive capacity (T)
	1.0–0.1	0.1–0.02	0.02–0.002	< 0.002					[mmol(+) · kg^{-1}]	
Sandy	80	14	2	4	3.9	5	8.67	35.8	0	35.8
Loess	1	63	27	9	4.3	21.3	20.05	41.7	30	71.7
Loamy	29	19	34	18	5.6	17	49.09	9.2	332.4	341.6

The surfactant used in the experiments was hyamine 1622 (molar mass = 448.1 $g \cdot mol^{-1}$, CMC = $2.75 \cdot 10^{-3}$ $mol \cdot dm^{-3}$ [9]) produced by Sigma-Aldrich (Germany). It is a cationic surfactant with the following chemical formula:



The properties of surfactants depend on the CMC, it is a concentration at which they begin to form aggregates. The form in which the surfactant is in solution (monomeric or aggregated) affects its sorption. For this reason, solutions of hyamine with concentrations below and above the CMC were studied.

The sorption experiments were performed under static conditions: 2 grams of soil were added to 10 cm^3 of water solution of hyamine with required concentration (0.00015, 0.0003, 0.0005, 0.001, 0.0015, 0.002, 0.003, 0.004, 0.005 and 0.006 $mol \cdot dm^{-3}$) and shaken for 6 hours at room temperature. After that time the soil suspensions were centrifuged at 4000 rev. $\cdot$ min^{-1} for 20 minutes to separate the liquid phase from the solid phase. Next, a part of the solution taken from above the solid phase of the soil was transferred to polyethylene test tubes and analysed for the presence of hyamine. The level of the surfactant in the solutions was determined with the technique of *high performance liquid chromatography* (HPLC) using a Hypersil Gold RP-C_{18} column and an UV-VIS detector at $\lambda = 269$ nm. The mobile phase was a system of solvents – acetonitrile/water (95/5, v/v) in an acetate buffer with pH 7.4. Flow rate of 0.5 $cm^3 \cdot min^{-1}$ was applied. The amount of hyamine sorbed by the soil (q, [$mol \cdot kg^{-1}$]) was calculated from the formula:

$$q = (C_o - C_{eq}) \cdot V/m \qquad (1)$$

where: C_o and C_{eq} – initial and equivalent concentrations of surfactant [$mol \cdot dm^{-3}$],
V – volume of the solution [dm^3],
m – mass of the soil [kg].

The sorption of hyamine was also conducted from solutions with pH 3, 4, 5, 6, 7, 8 and with constant concentration of the surfactant – 0.005 $mol \cdot dm^{-3}$. The pH of the solutions was controlled through dosage of NaOH (1 $mol \cdot dm^{-3}$) or HCl (1 $mol \cdot dm^{-3}$). The use of NaOH and HCl solutions at concentration of 1 $mol \cdot dm^{-3}$ meant that the initial water solutions of were excessively diluted. Whereas, pH control by means of 0.1 mol solutions NaOH and HCl would require the dosage of correspondingly larger amounts of the solutions. The effect of KCl and KNO_3 on the sorption of hyamine was studied at the surfactant/electrolyte molar ratios of 1 : 1 and 1 : 10. In the solutions with electrolytes the concentrations of hyamine were from 0.00015 to 0.006 $mol \cdot dm^{-3}$. The time required to reach sorptive equilibrium was determined through shaking 2 g samples of the soils from 10 cm^3 of hyamine solution with concentration of 0.006 $mol \cdot dm^{-3}$ during 15, 30, 60, 180, 300, 360, 480, 600 and 720 minutes.

The interpretation of results of the sorption kinetics was performed based on a pseudo second-order equation:

$$t/q_t = 1/k_2 \cdot q_{eq}^2 + t/q_{eq} \tag{2}$$

where: q_t – amount of sorbate sorbed during time t [$mol \cdot kg^{-1}$],
t – time [min],
k_2 – second order rate constant [$kg \cdot mol^{-1} \cdot min^{-1}$],
q_{eq} – amount of sorbate sorbed at equilibrium [$mol \cdot kg^{-1}$].

All experiments were made in three replications.

Results

Figure 1 presents changes in the level of hyamine sorption in relation to equivalent concentration. In the loamy soil the sorption of hyamine varied from 0.00075 $mol \cdot kg^{-1}$ to 0.03 $mol \cdot kg^{-1}$, which constituted 100 % of the content of the surfactant in all initial solutions.

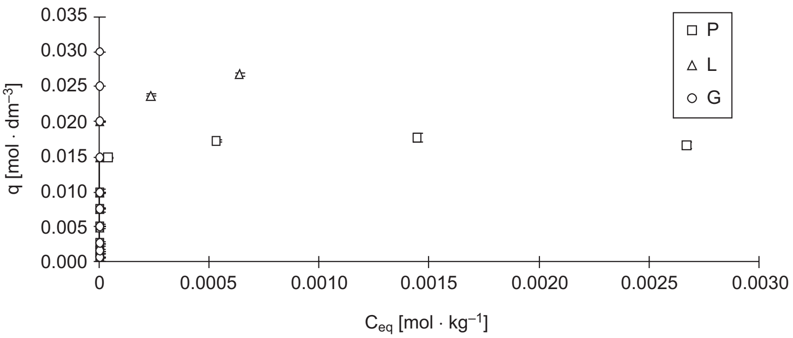


Fig. 1. Isotherms of the hyamine sorption in sandy soil (P), loess soil (L) and loamy soil (G); q – equilibrium sorption capacity; C_{eq} – equilibrium concentration; Error bars represent standard deviation of triplicate assays (shown if larger that the symbols)

The maximum, 100 % degree of sorption was found also in the sandy soil for initial concentrations from 0.00015 to 0.002 $mol \cdot dm^{-3}$, and in the loess soil for concentrations in the range of 0.00015–0.004 $mol \cdot dm^{-3}$. In the sandy soil, at equivalent concentration of $1.45 \cdot 10^{-3}$ $mol \cdot dm^{-3}$, the sorption reached a maximum of 0.0178 $mol \cdot kg^{-1}$ and then dropped to the level of 0.0167 $mol \cdot kg^{-1}$ at concentration of $2.67 \cdot 10^{-3}$ $mol \cdot dm^{-3}$. Whereas, in the loess soil a gradual increase of hyamine sorption was observed up to a maximum level of 0.0268 $mol \cdot kg^{-1}$ at equivalent concentration of $6.36 \cdot 10^{-4}$ $mol \cdot dm^{-3}$.

Analysis of the kinetic data (Fig. 2A) indicates that in the sandy and loess soils the intensity of the sorption was high already at the initial stage of the process. In the 15th

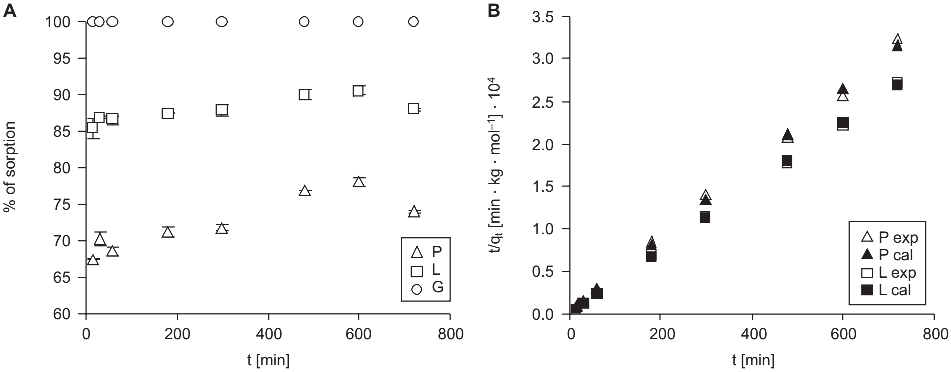


Fig. 2. A: Kinetics of hyamine sorption in sandy soil (P), loess soil (L) and loamy soil (G); B: Comparison between experimental (exp) and calculated (cal) values of t/q_t versus time (t) for the sorption of hyamine in sandy (P) and loess (L) soil; q_t – amount sorbed after time t; Error bars represent standard deviation of triplicate assays (shown if larger that the symbols)

minute the sorption was at the level of 0.0202 $\text{mol} \cdot \text{kg}^{-1}$ in the sandy soil and 0.0256 $\text{mol} \cdot \text{kg}^{-1}$ in the loess soil. Relative to the initial content of hyamine in the solution, that constituted 67.5 and 85.4 %, respectively. However, the effectiveness of the sorption changed only slightly with the passage of time of the contact between the initial solution and the sandy and loess soils. For example, after 60 and 300 minutes the following values of the sorption were obtained: 0.0205 and 0.0215 $\text{mol} \cdot \text{kg}^{-1}$ for the sandy soil, and 0.026 and 0.0263 $\text{mol} \cdot \text{kg}^{-1}$ for the loess soil. Compared with the sorption level on the 15th minute, after 60 and 300 minutes the sorption increased by 0.8 and 4.2 % in the sandy soil, and by 1.3 and 2.3 % in the loess soil. In the loamy soil the sorption was 0.03 $\text{mol} \cdot \text{kg}^{-1}$ (100 % of the initial content in the solution) and did not depend on the duration of the soil-solution contact.

The results of kinetic studies were analysed using the pseudo second-order model. The second order rate constant, k_2, and the amount of hyamine sorbed at equilibrium, q_{eq}, were obtained from the slope ($1/q_{eq}$) and the intercept ($1/k_2 \cdot q_{eq}^2$) of the linear plot of experimental data of t/q_t versus t. Average values of k_2 and q_{eq} were as follows: $k_2 = 80.1 \cdot 10^{-5}$ $\text{kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$, $q_{eq} = 229$ $\text{mol} \cdot \text{kg}^{-1}$ for sandy soil and $k_2 = 276 \cdot 10^{-5}$ $\text{kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$, $q_{eq} = 267.9$ $\text{mol} \cdot \text{kg}^{-1}$ for loess soil. The kinetic parameters k_2 and q_{eq} were used to calculate theoretical values of q_t by application the equation 2. Fig. 2B shows the comparison between the experimental data and calculated data, which are obtained from the pseudo second-order equation. It is apparent from Fig. 2B, that the calculated data were similar to the experimental data or were the almost the same. This may indicate that the sorption of hyamine followed in accordance with the pseudo second-order reaction mechanism. Fig. 2B does not present the relation q_t/t in the function of time for sorption in the loamy soil due to the lack of any effect of time on hyamine sorption in that soil.

Figure 3 presents the relation of hyamine sorption in the soils in the function of pH values of the initial solution. It can be concluded that increase in pH value did not cause

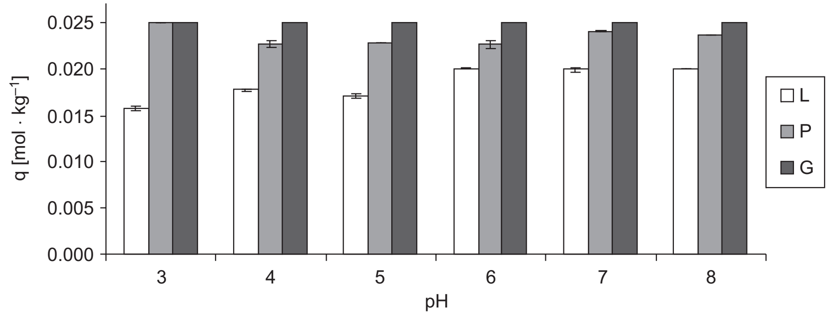


Fig. 3. Sorption of hyamine from solution of different pH in sandy soil (P), loess soil (L) and loamy soil (G); q – equilibrium sorption capacity; Error bars represent standard deviation of triplicate assays (shown if larger that the symbols)

any change in the level of hyamine sorption in the loamy soil. In the case of the loess soil, a slight decrease of hyamine sorption was observed within the range of pH 4 to pH 8. In the case of the sandy soil, increase in pH resulted in a slight increase of sorption until a constant level was reached within the pH range from 5 to 8.

The results of experiments concerning the sorption of hyamine from solutions with an addition of KCl are presented in Fig. 4. In the sandy soil the effect of KCl was bidirectional. At the molar ratio of 1 : 1, a decrease of hyamine sorption from solutions with concentrations of 0.002–0.005 mol · dm^{-3} was observed relative to the solutions without KCl. Whereas, for the highest initial concentration an increase of the sorption by 11.5 % was noted. Also in the case of solutions with the molar ratio of 1 : 10 a similar direction of changes in the level of sorption was observed, ie a decrease by 4 %

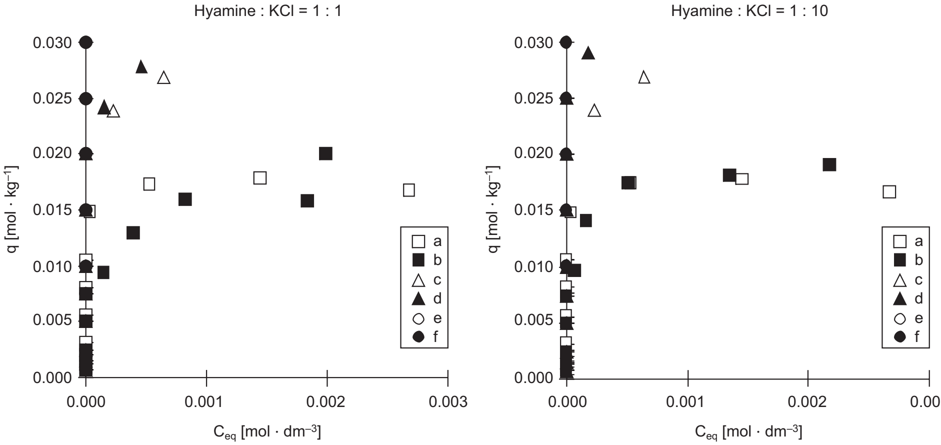


Fig. 4. Effect of KCl on the sorption of hyamine in sandy soil (a – without KCl, b + KCl), loess soil (c – without KCl, d + KCl) and loamy soil (e – without KCl, f + KCl); q – equilibrium sorption capacity; C_{eq} – equilibrium concentration; Error bars represent standard deviation of triplicate assays (shown if larger that the symbols)

for concentrations of 0.002–0.003 mol · dm^{-3} and an increase by 8.5 % for the concentration of 0.006 mol · dm^{-3}.

The effect of KCl on hyamine sorption in the loess soil was observable in the case of solutions with the highest initial concentrations: 0.005 and 0.006 mol · dm^{-3} (Fig. 4). At both molar ratios of the surfactant to the electrolyte, ie 1 : 1 and 1 : 10, an increase of hyamine sorption was observed relative to the sorption from solutions without any addition of KCl. The greatest changes were noted for sorption from the solutions with the molar ratio of 1 : 10.

The sorption of hyamine at that molar ratio from the solution with concentration of 0.005 mol · dm^{-3} was higher by 4.8 % with relation to the sorption from solution without any content of KCl. For the solution with concentration of 0.006 mol · dm^{-3} the increase in sorption was higher at 7.8 %.

The effect of KNO_3 on the sorption of hyamine in the sandy and loess soils had a character similar to that of the effect of KCl in the sandy soil (Fig. 5).

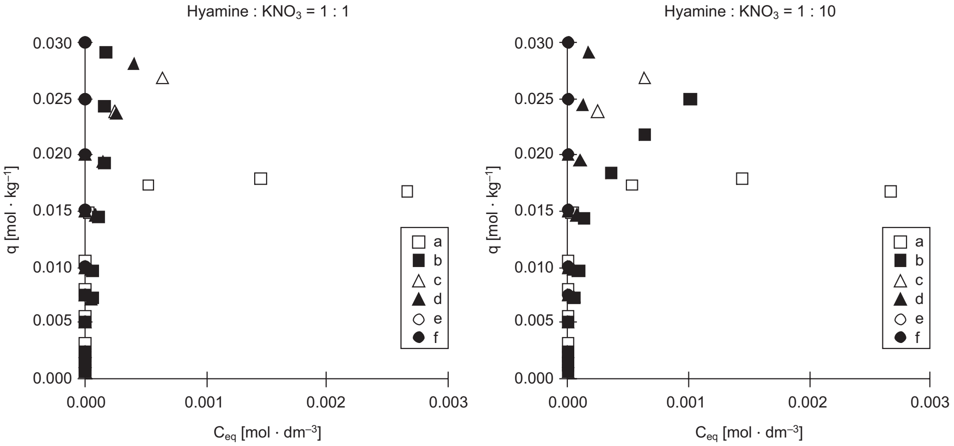


Fig. 5. Effect of KNO_3 on the sorption of hyamine in sandy soil (a – without KNO_3, b + KNO_3), loess soil (c – without KNO_3, d + KNO_3) and loamy soil (e – without KNO_3, f + KNO_3); q – equilibrium sorption capacity; C_{eq} – equilibrium concentration; Error bars represent standard deviation of triplicate assays (shown if larger that the symbols)

At the surfactant/electrolyte molar ratios of 1 : 1 and 1 : 10 a decrease of sorption in the sandy soil was noted for initial concentrations from 0.0015 to 0.003 mol · dm^{-3}, and in the loess soil also for the concentration of 0.004 mol · dm^{-3}. It should be emphasised that the decrease was slight and did not exceed 4.5 % in the sandy soil and 3.5 % in the loess soil. In the range of concentrations from 0.004 to 0.006 mol · dm^{-3} an increase of sorption was observed in the sandy soil, from 10.3 to 41.6 % at the molar ratio of 1 : 1, and from 4.7 to 27.8 % at the ratio of 1 : 10. In the loess soil a notably smaller increase was noted (a maximum of 7.9 %) for initial concentrations of 0.005 and 0.006 mol · dm^{-3}.

In the loamy soil the presence of KCl and KNO_3 did not cause any change in the level of hyamine sorption (Figs. 4 and 5). In this system, as in the case of sorption from the solutions without any electrolyte, the level of sorption from all initial solutions was 100 %.

Discussion

The form of isotherms of hyamine sorption from the soils under study conforms to that of isotherms type L and H acc. to the classification by Giles and indicates strong interactions between hyamine and the soils [10]. This is supported by the 100 % sorption of hyamine from all solutions in the loamy soil, and by the high levels of hyamine sorption in the sandy and loess soils both from solutions with low and with medium initial concentrations of the surfactant. Also the results of the kinetic tests, and especially the high level of sorption in the initial phase of the experiment, suggest high affinity of hyamine to the soils used in the study. The sorptive properties of the studied soils with relation to hyamine were, however, notably varied, as indicated by the various forms of the isotherms in the area of high equivalent concentrations. Such behaviour of surfactants is frequently observed in soils with a high level of clay minerals and a relatively low organic matter content (< 5 %) [11]. The soils used in this study were characterised by a low content of organic carbon (below 3 %) and distinctly varied levels of clay fractions. It should be emphasised that the sequence of affinity to hyamine, determined on the basis of sorption levels, coincided with the hierarchy of the soils in the order of increasing content of clay fractions: sandy soil < loess soil < loamy soil. This sequence is also in agreement with the sorptive capacity of the soils under study.

The study demonstrated that in the sandy and loess soils the intensity of the sorption from solutions with higher initial concentrations was distinctly lower compared with that from solutions with lower concentrations. Xu and Boyd [12] presented the opinion that cationic surfactants are bound by soils in an alternating manner. Sorptive sites with negative charge attract the positively charged “head” of the surfactant, while its non-polar “tail” is oriented towards the soil solution. With increase in the concentration of the solution more and more sorptive sites are fitted in this way with the surfactant ions. It can be assumed that in the sandy soil, with lower sorptive capacity relative to the loess soil, saturation of the sorptive sites proceeded faster. For this reason, for solutions with the highest initial concentrations only slight changes were observed in the level of hyamine sorption in the sandy soil.

The lower sorption of hyamine from the solution with concentration of 0.006 $mol \cdot dm^{-3}$ observed in the sandy soil relative to the solution with concentration of 0.005 $mol \cdot dm^{-3}$ could be a result of electrostatic repulsion between the positively charged “heads” of the polar part of the surfactant [4]. As a result of that, hyamine cations were forced away from the active surface of the soil sorbents into the soil solution. Consequently, hyamine ions had difficult access to the sorptive sites and, therefore, the sorption of the surfactant decreased. With increase of the concentration of the solution, the forces of repulsion increase as diminish the distances between equally charged ions of the surfactant. This explains why a decrease of hyamine sorption was observed in the case of the solution with the highest concentration.

Analysis of the results revealed that the process of hyamine sorption in the loamy soil did not depend on the pH of the initial solution, and in the case of the sandy and loess soils the effect of pH of the solution on the sorption of the surfactant was slight. This should be attributed to the considerably stronger buffering properties of the loamy soil compared with the weaker regulating properties of the sandy and loess soils, resulting from the physicochemical properties of the soils studied.

Based on the study presented here it can be stated that the effect of electrolyte on the sorption of hyamine, or the lack of it, was related with the sorptive capacity of the soils used in the study. In the sandy and loess soils two opposite effects were observed, ie a decrease and an increase in the presence of an electrolyte with relation to sorption from solutions with no content of KCl or KNO_3. It should be noted that no such effect was found in the loamy soil, with the highest sorptive capacity, where the sorption of hyamine was total from all the solutions. Studies by Bouchard et al [13] and Brownawell et al [14] indicate that surfactant ions sorbed by a soil may be exchanged for cations of an electrolyte present in the solution. This would suggest that competition for sorptive sites between hyamine cations and K^+ ions could had been the cause of reduced sorption of the surfactant in the sandy and loess soils. That effect was less pronounced in the loess soil due to its higher sorptive capacity. Whereas, the increased sorption of hyamine in the presence of the electrolytes could have been caused by the compression of the positive charge of the "heads" of hyamine by anions Cl^- and NO_3^-. The result of that was a reduction of the mutual repulsion of hyamine cations, which stimulated the process of sorption in the soils [15].

Conclusions

1. The level of hyamine sorption was related to the sorptive capacity of the soils and basically increased with increasing concentration of the initial solution.
2. In the sandy and loess soils the effectiveness of hyamine sorption displayed slight changes with extension of the time of sorption and with increase in the pH of the initial solution. In the loamy soil the sorption of hyamine was at a constant level irrespective of the time of contact of the soil with the solution and of the pH of the solution.
3. The presence of an electrolyte did not cause any change in the level of hyamine sorption in the loamy soil. In the sandy and loess soils the effect of electrolytes on the sorption of hyamine depended on the kind of electrolyte used, on the sorptive capacity of the soil, and on the concentration of the surfactant.

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SORPCJA SURFAKTANTU HIAMINY 1622 W GLEBACH

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Abstrakt: Badano sorpcję hiaminy 1622, kationowego surfaktantu, z wodnych roztworów w 3 glebach, które ze względu na charakter skał macierzystych, nazwano w pracy odpowiednio glebą piaszczystą, lessową i gliniastą. Proces sorpcji prowadzono metodą statyczną: do probówek z polietylenu odważano 2 g gleby i dodawano 10 cm^3 roztworu o stężeniu hiaminy w zakresie od 0,00015 do 0,006 $mol \cdot dm^{-3}$, a następnie wytrząsano przez 6 godz. Określono wielkość sorpcji hiaminy w zależności od stężenia i pH roztworu wyjściowego, czasu kontaktu gleba – roztwór oraz w obecności elektrolitów KCl i KNO_3 w układach surfaktant-elektrolit = 1 : 1 i 1 : 10.

Badania wykazały, że ze wzrostem stężenia roztworu wyjściowego następowało zwiększenie sorpcji hiaminy w glebach. Ustalono, że szereg powinowactwa badanych gleb względem hiaminy układał się następująco: gleba gliniasta > gleba lessowa > gleba piaszczysta. Wraz ze wzrostem pH obserwowano niewielkie zmiany efektywności sorpcji w glebie piaszczystej i lessowej, natomiast w glebie gliniastej sorpcja utrzymywała się na stałym poziomie. Badania kinetyczne wykazały, że w glebie piaszczystej i lessowej sorpcja zachodziła najszybciej w ciągu pierwszych 15 min, a wydłużenie czasu kontaktu gleba–roztwór do 720 min nie powodowało wyraźnych zmian w poziomie sorpcji. W glebie gliniastej stwierdzono 100 % stopień sorpcji hiaminy niezależnie od czasu kontaktu roztworu z glebą. Proces sorpcji zachodził zgodnie z mechanizmem reakcji pseudodrugiego rzędu. Obecność elektrolitu powodowała zarówno zmniejszenie, jak i zwiększenie sorpcji hiaminy w glebie piaszczystej i lessowej, ale w stopniu zależnym od rodzaju elektrolitu oraz stężenia surfaktantu. Dodatek elektrolitu nie wpływał na sorpcję hiaminy w glebie gliniastej.

Słowa kluczowe: surfaktant kationowy, sorpcja, gleba

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CONTENT OF SELENIUM IN ALFALFA IN DEPENDENCE OF ITS DOSE AND THE TYPE OF SOIL

ZAWARTOŚĆ SELENU W LUCERNIE W ZALEŻNOŚCI OD JEGO DAWKI I TYPU GLEBY

Abstract: The aim of research was the assessment of the effect of selenium addition to soils of diversified granulometric composition (light loamy sand, light loam and clay silt) on the yielding and Se content in alfalfa harvested twice in the course of plant growing period. Selenium was introduced in the following doses: 0, 20, 40 and 60 $\mu g \cdot kg^{-1}$ of soil in the form of water solution of Na_2SeO_3.

The addition of selenium to light loamy sand in the amount of 20 and 40 $\mu g \cdot kg^{-1}$ of soil did not affect alfalfa yielding, while the dose of 60 $\mu g \cdot kg^{-1}$ resulted in decreased quantity of biomass harvested. Significantly higher yield, in comparison with the one obtained from control treatments and fertilized with the remaining Se doses, was determined for cultivation conditions involving light loam supplemented with 20 $\mu g \cdot kg^{-1}$ of this element and with 60 $\mu g \cdot kg^{-1}$ in the case of silty soil. Selenium content in plants increased according to gradually higher doses of this element, yet only on light loam supplemented with selenium dose of 60 $\mu g \cdot kg^{-1}$ it reached the level meeting animals' needs regarding this microelement.

The properties of the examined soils and introduced selenium doses differentiated availability of this element for plants. The higher quantity of selenium applied as fertilizer, the higher amount of this element passing into both extracts and Se-DTPA content was twice higher than that of Se-HCl. The content of selenium in alfalfa did significantly depend on total content of this component in the soil, as well as on the amount of DTPA and HCl (1mol $\cdot$ dm^{-3} concentration) – extracted Se forms.

Keywords: selenium, alfalfa, soil type

Investigation conducted recently proved that in the area of Poland a considerable share belongs to soils featuring low content of selenium [1–8]. Additionally, significant soil acidification can be the cause of poor uptake of this microelement by plants [9–13].

Selenium is classified to indispensable elements regarding animals feeding, especially carnivores [5, 10, 14]. Yet constantly maintained sale of feeds characterizing insufficient selenium content can lead to the occurrence of numerous diseases in

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animals, including diminished fertility, the increased number of miscarriages or food muscular dystrophy. High degree of selenium absorption from feeds and a slight difference between optimum and toxic quantity bring about the necessity of preceding any supplementation of this element by precise estimation of selenium resources in soils, also taking into account the factors conditioning its availability for plants and the ability of its accumulation featuring particular species [15].

The aim of the research was determination of selenium in alfalfa in relation to soil suitability classification and microelement dose applied.

Material and methods

The assessment of the effect of selenium dose on alfalfa yielding and accumulation of this element was based on the results of pot experiment established in pots of Wagner's type, whose volume amounted to 5.0 kg of air-dry soil. Investigation involved three types of soil, differing in their granulometric composition: *light loamy sand* (lls), *light loam* (ll) and *clay's silt* (cs). Selected soil properties were shown in Table 1.

Table 1

Selected properties of soils

Soil textural group	Share [%] of fraction < 0.02 mm	pH_{KCl}	CEC [cmol(+) $\cdot$ kg^{-1}]	org-C [g $\cdot$ kg^{-1}]	Se [μg $\cdot$ kg^{-1}]		
					Total	DTPA	HCl
Light loamy sand (lls)	12	3.7	4.4	12.5	92	6.0	7.5
Light loam (ll)	21	4.8	8.8	24.1	143	13.8	16.1
Clay's silt (cs)	41	6.7	27.0	23.5	180	16.0	17.5

CEC – *cation exchangeable capacity*; Se-DTPA and Se-HCl – selenium form extracted by DTPA (*Diethylene Triamine Pentaaceric Acid*) and 1 mol $\cdot$ dm^{-3} HCl solution, respectively.

Because of strongly acidic reaction of soil containing light loamy sand and acidic reaction of light soil, as far as its granulometric composition was concerned, the soils underwent liming with $CaCO_3$ in the dose being an equivalent of 1.0 hydrolytic acidity. After balancing soil moisture of all the samples to 60 % of their maximum water capacity, they were subjected to 14-day – incubation. Then there was applied basic mineral fertilization and selenium supplementation. Se was introduced in the form of water solution of Na_2SeO_3 in the doses of 0, 20, 40 and 60 μg Se $\cdot$ kg^{-1} d.m. of soil. The latter ones were determined so that the content of this element did not exceed the range assumed for soils belonging to particular granulometric groups, which was confirmed by earlier examination [6].

A test plant was alfalfa (*Medicago sativa*), 'Susi' cultivar. Plants biomass was harvested twice in the course of plant growing period, in the stage of flowering. All treatments were provided with the same mineral fertilization. Before sowing and after the first harvest of alfalfa there were applied the following compounds: 0.15 g N $\cdot$ kg^{-1} of soil (NH_4NO_3), 0.06 g P $\cdot$ kg^{-1} and 0.30 g K $\cdot$ kg^{-1} (K_2HPO_4 + KCl) and

0.03 g Mg · kg^{-1} ($MgSO_4 \cdot 7H_2O$). In both cultivation terms fertilization with phosphorus, potassium and magnesium was introduced twice, while nitrogen was used in three equal doses (each amounting 0.05 g N · kg^{-1} of soil). Harvested plant material, dried at room temperature was subjected to determination of selenium content by AAS method, accompanied by hydride generation using Spectr AA 220FS Varian device with VGA-76 attachment after the samples had been prepared according to methodic described in Annex to Ordinance by Ministry of Agriculture and Development of Rural Areas dated on 23rd January 2003 [16].

There was assayed total selenium content in soil samples collected after experiment had been completed and decomposed in the mixture of HNO_3 + HCl + H_2O_2 on water bath at the temperature of 95 °C, then subjected to selenium reduction to Se(IV) through the addition of 6 mol HCl · dm^{-3} [17]. Selenium form available for plants was determined after DTPA soil extraction with the use of Lindsay and Norwell method [18] and after extraction by 1 mol · dm^{-3} HCl solution. All determinations, both in plant and soil material, were done in three replications, separately for each pot. Obtained results were statistically elaborated with the use of analysis of variance and Tukey test, at significance level p = 0.05, according to Statistica program.

Results and discussion

Total selenium content in soils used for examination did not differ from the values reported by Piotrowska [19] and also by Patorczyk-Pytlik and Kulczycki [6] for those granulometric groups (Table 1). In comparison with the values obtained by the mentioned authors, the examined soils characterized low total selenium content.

The amount of selenium in light soil, according to the values reported by Gupta and Gupta [10], should be accepted as a critical one regarding the quality of harvested yield. However, according to criteria assumed by Zablocki [20] after Welles, even lower Se content than 300 μg · kg^{-1} should be treated as deficit from the point of view of feed value of the cultivated plants. Similarly to the results obtained by numerous authors [2, 6, 7, 19–21] it was possible to confirm significant relation between selenium content in the soil and the content of silt and clay fraction.

The content of DTPA- and HCl-extracted selenium forms was conditioned by granulometric composition of the examined soils (Table 1). From 6.7 % to 9.6 % of total Se content in soils passed to DTPA solution, so those values were slightly higher than the ones determined by Borowska and Koper [3]. In soils investigated by the authors mentioned above, DTPA-soluble selenium forms provided for approximately 6 %. The quantity of Se passing to 1 mol · dm^{-3} HCl solution was higher than that determined in DTPA, as it ranged from 7.5 μg · kg^{-1} (8.2 %) to 17.5 μg · kg^{-1} (11.2 %). In both solutions the most considerable share of soluble Se forms characterized light loam (ll) while light loamy sand featured the lowest percentage of soluble Se (lls).

Conducted research proved that both alfalfa yielding and selenium content in this plant was conditioned by the category of soil suitability classification, as well as the dose of selenium (Table 2).

Table 2

Yield and content and uptake of selenium by alfalfa

Dose [μg Se · kg^{-1}]	Yield [g d.m. per pot]			Content [μg Se · kg^{-1}]		Uptake [μg Se per pot]		
	harvest I	harvest II	Σ	harvest I	harvest II	harvest I	harvest II	Σ
Light loamy sand (lls)								
0	14.7	17.9	32.6	11.5	12.2	0.16	0.22	0.38
20	13.5	19.1	32.6	21.6	22.2	0.29	0.42	0.72
40	13.5	19.2	32.7	33.8	43.6	0.45	0.84	1.29
60	12.6	16.9	29.5	62.2	59.0	0.79	1.00	1.78
Mean	13.6	18.3	31.9	32.3	34.3	0.42	0.62	1.04
Light loam (ll)								
0	16.7	20.8	37.5	7.2	16.8	0.13	0.35	0.48
20	18.6	21.9	40.5	25.1	31.2	0.52	0.62	1.14
40	15.8	20.8	36.6	61.1	59.0	0.95	1.22	2.18
60	16.8	20.2	37.0	94.6	87.5	1.60	1.77	3.36
Mean	17.3	20.4	37.7	47.2	48.6	0.80	0.99	1.79
Clay's silt (cs)								
0	11.2	18.3	29.5	20.6	16.9	0.23	0.31	0.54
20	11.8	17.7	29.5	33.4	31.4	0.42	0.56	0.98
40	12.6	17.2	29.8	46.9	47.0	0.59	0.81	1.40
60	13.4	18.6	32.0	61.4	61.5	0.82	1.15	1.97
Mean	12.3	17.9	30.2	41.1	39.2	0.52	0.70	1.23
LSD$_{0.05}$ Interaction soil × doses	2.4	1.4	3.2	11.7	4.4	0.37	0.12	0.43

In both harvests alfalfa yield was significantly higher for alfalfa cultivation on medium-heavy soil than on the remaining soils. On all the soils markedly higher amount of alfalfa biomass, both from control treatments and from the treatments fertilized with selenium, was harvested in the second cutting. Introduction of 20 and 40 μg Se · kg^{-1} to light loamy sand (lls) did not diversify alfalfa yield size harvested in the first term, while it resulted in yield increase in the second cutting, as compared with the quantity of biomass obtained from control treatment. The highest Se dose (60 μg · kg^{-1}) in both terms resulted in the decrease in alfalfa biomass amount in relation to that harvested from control treatment, as well as to the treatments where lower doses of this element were applied.

Significantly higher biomass yield, as compared with control treatment and the treatments fertilized with the remaining Se doses, was recorded for medium-heavy soil (ll) under the influence of 20 μg Se · kg^{-1} and for heavy soil (cs) after introduction of 60 μg Se · kg^{-1}. Advantageous effect of low selenium doses on plants growth and development was also proved by Hartikainen et al [22], Xue et al [23] and Hawrylak-Nowak [24]. In plants classified as "not accumulating Se", high content of this element in their tissues do negatively affect synthesis of proteins [15], reduces starch content [25], increases phosphorus and calcium content and diminishes the quantity of potassium [24].

Selenium does not belong to chemical elements recognized as indispensable ones regarding growth and development of majority of cultivated plants, although when growing on soils featuring high Se content, plants can accumulate considerable amounts of this element [15, 22, 26, 27]. Positive significant correlation between total selenium content in soils and the quantity of this element in alfalfa was also confirmed by other authors [1, 2, 13, 20].

Trafikowska and Kuczynska [8] report that alfalfa harvested from cultivated fields in the region of Bydgoszcz, contained, on average, 34 μg Se $\cdot$ kg^{-1} d.m. Se contents obtained in our investigation point to the fact that alfalfa harvested from soils not fertilized with selenium contained lower amounts of this element (Table 2), as it ranged from 7.2 μg to 20.6 μg Se $\cdot$ kg^{-1} d.m. Judging from the point of view of animals nutrition, the mentioned Se amount should be regarded as deficit [5, 10, 14].

Applied selenium doses caused the increase in this microelement in aboveground parts of alfalfa cultivated on all the types of soils, yet Se content meeting optimum value, as far as animals nutrition is concerned, was recorded only in plants cultivated on light loam supplemented with 60 μg Se $\cdot$ kg^{-1} of soil.

In the first alfalfa harvest originating from control treatment significantly higher selenium content characterized plants cultivated on heavy soil (cs), while the lowest – on medium-heavy soil (ll). In plants coming from the second harvest, Se content in alfalfa cultivated on medium-heavy and heavy soil featured similar values. The latter ones were significantly higher than Se content determined in alfalfa growing on light soil. Similar relation involved alfalfa cultivated on soils supplemented with 20 μg Se $\cdot$ kg^{-1}. At higher doses of selenium (40 and 60 μg Se $\cdot$ kg^{-1}), in plants originating from both cuttings, the highest Se content was determined when plants were growing on medium-heavy soil (ll). This dependence was also observed for the quantity of selenium absorbed by alfalfa. Poorer ability of selenium uptake characterized plants originating from sandy soils, in comparison with those cultivated on loamy and silty soils, was also reported by Yläranta [21], Laser [12] and Dhillon et al [9], while Johnson [11] obtained reversed relation.

The properties of the examined soils, selenium dose and alterations this element underwent in soils in the course of plant growing period diversified solubility of Se forms in DTPA and 1 mol $\cdot$ dm^{-3} HCl solution (Table 3). In soil samples collected from control treatments the share of extracted Se forms was lower than that determined in the soils before experiment was established (Table 1). Evidently lower decrease in available Se forms, especially in light loamy sand, comparing with the remaining soils, indicates that intensive sorption process of introduced selenate(IV) does take place in these soils [26]. As the quantities of introduced selenium increase, there also increase the amount of this element passing to both extractors and the content of DTPA-extracted Se forms was approximately twice higher than that of 1 mol $\cdot$ dm^{-3} solution of HCl-extracted Se forms.

Table 3

Total selenium content and the content of Se forms extracted by DTPA and by 1 mol · dm^{-3} HCl solution in soils collected after alfalfa

Dose	Content of Se		Share of Se-DTPA* in total Se	Content of Se-HCl*	Share of Se-HCl in total Se
	Total	DTPA			
[μg Se · kg^{-1}]	[μg Se · kg^{-1}]		[%]	[μg Se · kg^{-1}]	[%]
Light loamy sand (lls)					
0	90	5.7	6.3	3.7	4.1
20	106	9.2	8.7	6.8	6.4
40	129	12.0	9.3	8.9	6.9
60	142	18.3	12.8	10.6	7.5
Mean	117	11.3	9.3	7.5	6.2
Light loam (ll)					
0	139	7.0	5.0	6.9	5.0
20	164	9.8	6.0	9.0	5.5
40	182	12.3	6.8	13.2	7.3
60	202	18.1	9.0	16.3	8.1
Mean	171	11.8	6.7	11.3	6.5
Clay's silt (cs)					
0	178	9.2	5.2	5.8	3.3
20	208	12.8	6.2	7.1	3.4
40	231	15.6	6.8	9.1	3.9
60	259	25.3	9.8	11.8	4.6
Mean	219	15.7	7.0	8.4	3.8
$LSD_{0.05}$ Interaction soil × doses	11.9	0.25		0.89	

Se-DTPA and Se-HCl – selenium form extracted by DTPA and HCl of 1 mol · dm^{-3} concentration, respectively.

Statistical analysis proved that selenium content in both alfalfa harvests and uptake of this elements by plants did significantly depend on total Se content in soils, as well as on the content of DTPA and HCl of concentration 1 mol · dm^{-3} – extracted selenium (Table 4).

Table 4

Correlation coefficients between Se content in alfalfa and its total content, as well as Se content extracted from soils by DTPA and HCl

Harvest	I harvest	II harvest	Total uptake
Total Se	0.55	0.53	0.49
Se-DTPA	0.79	0.80	0.69
Se-HCl	0.51	0.49	0.46

Significant at $p < 0.05$.

Conclusions

1. Introduction of 60 μg Se · kg^{-1} of soil did negatively affect the field of alfalfa cultivated on light loamy sand (lls), while it increased the quantity of alfalfa biomass originating from silty soil (cs). On light loamy soil, the best effect, expressed by alfalfa field size, was obtained from the treatment with Se supplemented soil in the dose of 20 μg · kg^{-1}.

2. As selenium dose increased, there also increased the content and amount of this microelement uptaken by alfalfa. The highest quantity of Se was absorbed by plants cultivated on light loamy soil, while the lowest uptake featured plants originating from light loamy sand.

3. Optimum feed value, regarding Se content, characterized alfalfa growing on light loamy soil fertilized with Se dose of 60 μg · kg^{-1}.

4. Selenium content in both alfalfa harvests did significantly depend on the properties of the soil used, including total Se content, as well as the amount of Se extracted by DTPA and HCl of 1 mol · dm^{-3} concentration.

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ZAWARTOŚĆ SELENU W LUCERNIE W ZALEŻNOŚCI OD JEGO DAWKI I TYPU GLEBY

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Abstrakt: Celem przeprowadzonych badań była ocena wpływu dodatku selenu do gleb o zróżnicowanym składzie granulometrycznym (piasku gliniastego lekkiego, gliny lekkiej oraz pyłu ilastego) na plonowanie oraz zawartość Se w lucernie, zbieranej dwukrotnie w okresie wegetacji. Selen zastosowano w dawkach: 0, 20, 40 i 60 μg · kg^{-1} gleby w postaci roztworu wodnego Na_2SeO_3.

Dodatek selenu do piasku gliniastego lekkiego w dawkach 20 i 40 μg · kg^{-1} gleby nie wpływał na plonowanie lucerny, natomiast 60 μg · kg^{-1} spowodowało obniżenie ilości zebranej biomasy. Istotnie większy plon niż określony dla roślin z obiektów kontrolnych oraz nawożonych pozostałymi dawkami stwierdzono w warunkach uprawy lucerny na glinie lekkiej pod wpływem 20 μg · kg^{-1}, a na glebie pylastej po zastosowaniu 60 μg · kg^{-1}. Zawartość selenu w roślinach zwiększała się wraz ze wzrostem dawki tego składnika, z tym że jedynie na glinie lekkiej z dodatkiem 60 μg · kg^{-1} kształtowała się ona na poziomie pokrywającym zapotrzebowanie zwierząt na ten mikroelement.

Właściwości użytych gleb oraz wielkość dawki selenu zróżnicowały dostępność tego pierwiastka dla roślin. Wraz ze wzrostem ilości selenu wprowadzonego do gleby zwiększała się ilość tego składnika przechodząca do obu ekstraktorów, z tym że zawartość Se-DTPA była około dwukrotnie większa niż Se-HCl. Zawartość Se w lucernie istotnie zależała od ogólnej zawartości tego pierwiastka w glebie, a także od zawartości form Se wyekstrahowanych przez DTPA oraz HCl o stężeniu 1 mol · dm^{-3}.

Słowa kluczowe: selen, lucerna, gatunek gleby

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Janina PIEKUTIN[1]

SURFACE WATER POLLUTED WITH PETROLEUM-DERIVATIVE SUBSTANCES IN PODLASIE REGION

ZANIECZYSZCZENIE WODY POWIERZCHNIOWEJ SUBSTANCJAMI ROPOPOCHODNYMI NA PODLASIU

Abstract: Subject of this work is to reveal the occurrence of petroleum-derivatives substances in surface water in Podlasie. Water samples were taken in test points localized on rivers cut by varied amount of traffic routes and roads with different surface quality. In water was determined: total suspension, COD_{Mn}, chlorides, sum of petroleum hydrocarbons, mineral oil index and lead.

The result of conducted research in water samples was content of petroleum-derivative substances expressed in mineral oil index and sum of hydrocarbons, lead and chlorides, high concentration of easily decomposable substances and variable suspension value. Presented material indicates problem's seriousness and proves necessity of making more.

Keywords: surface water, petroleum-derivative substances, motorization

The petroleum-derivative substances introduced into the environment origin mainly from motorization means, including private cars, city transport vehicles, cars for transporting products and services, city services, privileged, and agricultural vehicles. It is not possible to lower the number of these vehicles along with the industry, economics, and civilization development; worse – the number increases at a very fast rate.

Continuous increase of vehicles number, thus the traffic intensification, makes threats for large groups of people and natural environment growing [1]. A transit localization of Podlasie region (between Eurasian east and west) caused a road and rail transport more intensive, and in consequence, enhancing the risk of some threats. Due to insufficient road network or their insufficient technical parameters, Podlasie region is a bottleneck in a system of transit goods and passengers transport in this part of Europe. About 150 road and rail cisterns pass daily through the frontier crossings in Podlasie region. *International Road Transport* (TIR) and transport of dangerous materials, in

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practice is realized along all regional roads (7610 km in total) and is associated mainly with gasoline, diesel oil, and propane-butane supply to fuel distributors. About 1 200 000 Mg of dangerous substances (namely petroleum derivatives, although significant amounts of vinyl chloride and other more dangerous materials) are transported annually through Podlasie region roads.

Due to growing contamination of natural environment with petroleum-derivative hydrocarbons [1–4], it is necessary to consider the problem within frames of environmental and social medicine. The substances with recognized carcinogenic, neurotoxic, and embryotoxic properties, exert their influence on an organism not only suddenly, but also in chronic way, which is difficult to diagnose and prove. Most of hydrocarbons, after epoxidation or hydroxylation, is removed out of the organism through lungs. Unfortunately, some are accumulated in fat tissue and damage of internal organs can occur. Chronic exposure to petroleum-derivative contaminants (consumption of contaminated water and food) often leads to hormonal and hematopoietic processes [5].

The paper presents the status of petroleum and its derivatives contamination of selected surface waters. These results are a synthesis of author's own survey realized within frames of own research and available literature data.

Material and methods

Three rivers flowing through Podlasie region and localized as close to Bialystok as possible were selected to the survey. Water samples were collected from 10 points distributed on rivers: Suprasl, Narew, and Biala from September 2009 to February 2010. Two of these points were situated near busy streets of Bialystok (Kollataja and Produkcyjna Streets), other six – possibly close to high traffic roads near Bialystok, and other two – 1 km away from a road (national No. 8, 19, and 65, as well as regional No. 671 and 676) [6]. The water samples were collected in early autumn after heavy rainfall.

Collected water samples were subject to the following determinations: total sediments, $\mathrm{COD_{Mn}}$ (*chemical oxygen demand permanganate method*), chlorides, lead, sum of petroleum hydrocarbons and mineral oil index. All determinations were carried out in accordance with commonly accepted and recommended analytical procedures. Data presented in the paper are mean values from at least three replicates made simultaneously.

Results

Within seven years, total number of cars registered in Podlasie region increased by 50 % in relation to 2000. According to data of *System for Road Surface Assessment* (SOSN), about 12–13 % roads need to be renovated (ie being in very bad condition now) in Podlasie region (data for 2006–2007) [2, 4], while 62 % of national roads length in the region, are in good condition (Fig. 1).

Improvements of roads quality status cannot keep up with the increase of vehicles number, which in turn has negative consequences for the environment.

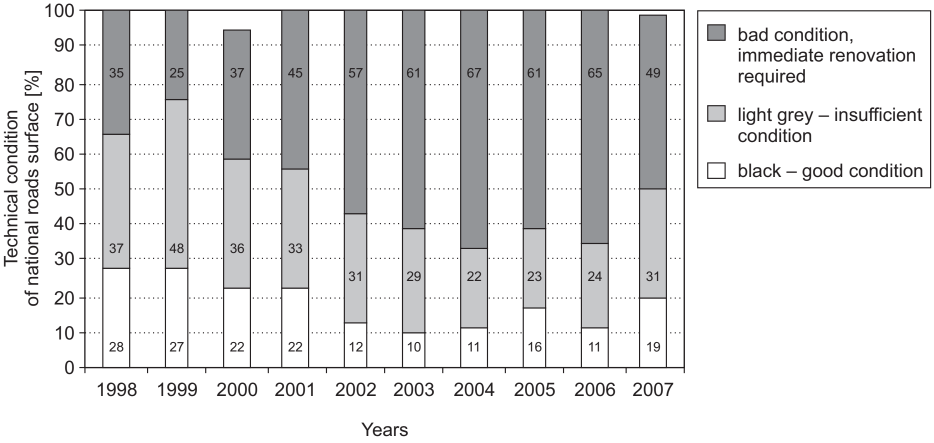

Fig. 1. Technical condition of national roads surface in Podlasie region in 1998–2007 according to SOSN

The largest amounts of mineral oils, 6.52 mg · dm^{-3} (Table 1), were determined in water sample No. 10 – Suprasl locality, Suprasl River. Such high level indicates the very bad technical status of mechanical vehicles, large traffic intensity, and poor road infrastructure. However, water in that river can be fast self-purified, because it contains large quantities of humus substances that increase the saturated hydrocarbons solubility about twice. Colloidal properties of humus substances imply that water pH and salinity changes may lead to their precipitation [1, 3].

Table 1

Quality of examined surface waters at selected sampling points (N = 10)

Sampling point									
1	2	3	4	5	6	7	8	9	10
Mineral oil index [mg · dm^{-3}]									
1.05	5.154	0.622	1.182	0.716	3.156	0.34	3.654	4.63	6.52
Lead [μg · dm^{-3}]									
24.01	39.6	20.22	21.39	21.39	26.8	20.67	37.14	34.88	26.8
Sum of petroleum-derivative hydrocarbons (C_6–C_{35}) [mg · dm^{-3}]									
0.02	0.14	0.02	0.01	0.01	0.11	0.05	0.07	0.09	0.12

Data presented in Table are mean values from three replicates; N – number of repetitions.

Samples No. 2, 6, 8, and 9 appeared to have high contents of mineral oils: oscillations ranged between 3.2 and 5.2 mg · dm^{-3}. All those samples were collected in places with high traffic intensity and dense infrastructure. Contents of mineral oils in other water samples ranged from 0.34 up to 1.2 mg · dm^{-3}. Points of those samples collection were much distant from high traffic and dense infrastructure. The examination revealed that about 70 % of samples, lead and petroleum-derivative hydrocarbons concentrations increased along with the increase of mineral oil index.

Determined concentrations of studied motorization contaminants indicates their migration into the surface waters, thus it should be supposed that their quantities are going to increase along with the traffic intensity rise [7, 8]. Despite of modern systems for collecting and purifying the rainfall water, there is a danger of environmental pollution during heavy and prolonged rainfalls, as well as during spring snow thawing, and penetrating contaminants into improperly sealed wells, melioration ditches, and sewage systems.

However, to counteract the contamination due to petroleum-derivatives, their quantities and behavior in water and soil environment should be recognized. Depending on physical properties of subsoil, contaminants flow along a surface or is infiltrated through the aeration zone into the water-carrying layer, and in consequence, it is adsorbed on rocky material, while the remaining part reaches the surface of a groundwater layer.

The technical condition of vehicles also considerably affects the scale of contaminants emission into the environment. The worse technical status of a vehicle, the more intensive negative effects on the environment it exerts. Unfortunately, facts referring to technical conditions of vehicles are alarming, because every third car driven over Polish roads is 16–30-years-old. About 300 000 new cars are sold annually in our country, while up to four times more used vehicles (about 1 200 000) are sold at the same period.

Among examined samples, the highest contents of suspensions (74 mg · dm^{-3}) were recorded in sample No. 1 – Fasty locality, Biala River (Fig. 2). The high content mainly resulted from the surface runoff from the road that is under bad technical condition and runoffs from adjacent cultivated fields, because the traffic intensity was quite low in that place. Point No. 7 – Bialystok, Produkcyjna Street, Biala River – was at the second rank in a view of suspensions amount. It is fairly crowded place in dense urbanized surroundings. The smallest suspension quantities were found at point No. 3 – Rzedziany, Narew River. Such low content of suspensions might result from a long distance to the road and low traffic intensity on a bridge that cuts the rivers. Other water

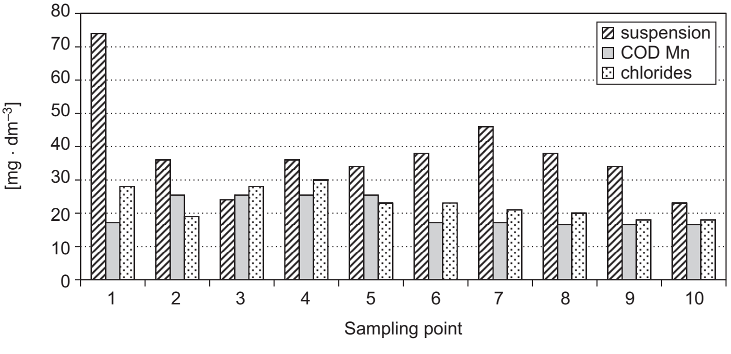

Fig. 2. Concentrations of some contaminants in studied water samples

samples revealed similar values of suspension contents within the range of 34–38 mg · dm^{-3}. Total suspensions originate mainly from the surface runoff from the infrastructure surrounding the road.

Discussion

Water from snow thawing, that flow out of the road surface in early spring, are contaminated very much, namely when the snow lies on the roadside for a longer time. Considerable contaminants accumulation occurs in a snow and ice, including large amounts of suspensions, lead, zinc, petroleum ether extractable substances (oils and other petroleum-derivative agents), and chlorides. High chlorides concentrations result from application the salt for slippery surfaces; hydrocarbons are not so easily decomposed in winter as during warm seasons, thus their contents can be also elevated. The largest runoffs of thawing snow water are present in spring with subsequent decrease till the complete snow and ice thawing [3, 4]. In the case of an excessive rainfall, light fractions of crude oil partially return to deeper layers or are washed out along with rain onto the ground surface and float on a water surface.

The water examining for COD_{Mn} values gives only the possibility to find out the readily-decomposable agents; however, if water contains petroleum-derivative substances, it would be reasonable to determine the COD_{Cr} (*chemical oxygen demand chromate method*) level, which is going to be made in nearest research.

Conclusion

Summing up, it can be concluded that the amounts of petroleum-derivative substances in surface waters of Podlasie region is significant what proves their migration from roads to surface water. Presented material only touches the problem and suggests the necessity of further and detailed studies upon that issue.

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ZANIECZYSZCZENIE WODY POWIERZCHNIOWEJ SUBSTANCJAMI ROPOPOCHODNYMI NA PODLASIU

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Abstrakt: Przedmiotem pracy są substancje ropopochodne w wodach powierzchniowych Podlasia. Próbki wody pobierano w punktach zlokalizowanych na rzekach przecinanych przez zróżnicowaną liczbę tras komunikacyjnych o kontrastowym natężeniu ruchu oraz trasy o różnej jakości nawierzchni. W wodzie oznaczano: zawiesinę ogólną, ChZT-Mn, chlorki, sumę węglowodorów ropopochodnych, indeks oleju mineralnego i ołów.

W wyniku przeprowadzonych badań w próbkach wody stwierdzono zawartość substancji ropopochodnych wyrażonych poprzez indeks oleju mineralnego i sumę węglowodorów, ołowiu i chlorków, duże stężenie substancji organicznych łatwo rozkładalnych i zmienną zawartość zawiesiny. Przedstawiony materiał sygnalizuje wagę problemu i dowodzi konieczności dalszych, szczegółowych badań w tym zakresie.

Słowa kluczowe: woda powierzchniowa, substancje ropopochodne, transport

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CONTENT OF COPPER, ZINC AND MANGANESE IN SOIL FERTILIZED WITH MUNICIPAL SOLID WASTE COMPOSTS

ZAWARTOŚĆ MIEDZI, CYNKU I MANGANU W GLEBIE NAWOŻONEJ KOMPOSTAMI Z ODPADÓW MIEJSKICH

Abstract: A three-year pot experiment has been conducted in order to analyze the influence of composts made from unsorted municipal solid waste and urban green waste on the total content of copper, zinc and manganese and their soluble forms in soil. The applied composts differed in maturity and the chemical composition of the matter from which they originated.

It has been found that the total content of copper, zinc and manganese in soil increased as the rates of municipal solid waste composts rose, an effect which has been observed both as a direct influence and aftereffect of fertilization. The highest increase in the total content of copper was determined in soil fertilized with six-month compost from municipal solid waste. By increasing doses of the compost, the share of the soluble form of this element was reduced versus its total content. The highest increase in total zinc appeared after soil amendment with compost which matured in a heap for three months. In respect of direct effect, the share of soluble to total zinc was the highest in the treatments fertilized with one-month compost, but as an aftereffect, six-month compost resulted in the highest percentage of soluble zinc in its total amount. As for manganese, evidently higher its total concentrations were determined in soil fertilized with three-month compost compared with one- and six-month ones. The share of the soluble form of manganese to its total content decreased when older municipal waste composts or their higher doses were applied.

In soil enriched with urban green waste, lower contents of heavy metals occurred than in soil fertilized with six-month compost. In the former soil, however, there was an increase in the share of soluble forms of the analyzed metals relative their total content.

Keywords: municipal solid waste compost, green waste compost, soil, copper, zinc, manganese

Municipal solid waste composts are used in agriculture as soil amending substances. Their chemical composition depends on a variety of factors, including the source of composted matter, the way it is composted and how long it is composted. A combination of these factors results in varied properties of produced composts [1, 2]. Among

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possible negative consequences of using composted municipal waste as a fertilizer is the risk of introducing heavy metals to the environment. This fact draws attention of many authors [3–6], who claim that the content of heavy metals in organic waste conditions the fertilizer value of many organic waste products.

Application of large doses of composts from municipal solid waste loaded with a high content of heavy metals causes a considerable increase in the total content of these elements in soil and subsequently in plants [7–8]. Thus, long-term application of municipal soil waste composts requires that the content of heavy metals in soil be regularly monitored [9].

Among some essential factors which determine the solubility of heavy metals in composts is the age of composted matter. Composting reduces soluble forms of heavy metals, which seems to suggest that the risk of heavy metals penetrating into the food chain decreases.

The content of heavy metals in composts is one of the criteria listed in the industrial standards (BN-88/9103) concerning composts. The standards establish allowable amounts of particular components in composts, which serve as a basis of assigning composts to particular quality classes [10].

The objective of this study has been to determine the direct and aftereffect of composts made from municipal solid waste and urban green waste on the total content of copper, zinc and manganese and their soluble forms in soil. The effect produced by the analyzed composts was compared with the action of a traditional organic fertilizer, such as farmyard manure.

Material and methods

The soil for the experiment originated from pot trials, which had been conducted in a greenhouse of the University of Warmia and Mazury in Olsztyn for three years. In the experiment, the direct and aftereffect of composts made from unsorted municipal solid waste according to the MUT-Dano technology on the content of total and soluble forms of copper, zinc and manganese in soil was studied. A more detailed description of the technological process for production of composts can be found in the authors' earlier paper [11].

The composts used in the experiment aged in heaps for 1, 3 or 6 months. These composts were introduced to soil in three doses: 10, 20 and 30 g $\cdot$ kg^{-1} of soil. The effect of municipal waste composts applied at the lowest rate (10 g $\cdot$ kg^{-1} of soil) was compared with the effect of an identical dose of compost made from urban green waste, which aged for six months, and that of *farmyard manure* (FYM). Rates of FYM were balanced with the lowest rate of municipal waste compost in terms of introduced *total nitrogen* (FYM_N) and *organic carbon* (FYM_C). Besides, in the treatments with the lowest doses of composts from municipal waste and FYM applied in the rate balanced with the composts with respect to the introduced nitrogen, additional mineral fertilization NPK was applied in the following quantities: 83 mg N $\cdot$ kg^{-1} soil, 26 mg P $\cdot$ kg^{-1} soil and 100 mg K $\cdot$ kg^{-1} soil. In the third year of the experiment, all the treatments received mineral fertilization in the rates of: 75 mg N $\cdot$ kg^{-1} soil, 31 mg P $\cdot$ kg^{-1} soil and

109 mg K · kg^{-1} soil. The characteristics of the soil used for the experiment were given in the authors' earlier paper [12]. Polyethylene Kick-Brauckamn pots were used for the experiment. They were filled with 10 kg of typical brown soil of the grain-size distribution of light loamy sand, and the pH KCl = 5.5, which was sampled from the humus layer Ap. Soil in the pots was maintained at a moisture level of 60 % field water capacity.

During the first year of the experiment, maize and sunflower were grown. Maize was harvested after 84 days of vegetative growth, in the panicle initiation phase and sunflower was collected after 61 days of growing, in the early inflorescence phase. In the second year, the crops included spring barley, harvested 57 days after sowing, in the stem elongation phase, and white mustard was gathered after 32 days of growing, in the full inflorescence phase. In the third year, lacy phacelia was grown, which was cut in the full inflorescence phase, corresponding to 61 days of vegetation.

The total content of heavy metals in the composts, farmyard manure and soil was determined with *the atomic emission spectrophotometric method with inductively activated plasma*, using an ICP-AES apparatus, model PS 950, manufactured by Labs, having first eluted samples of composts with a mixture of spectrally pure acids HNO_3 and $HClO_4$, mixed at a 5 : 4 ratio, in a VAL heat block. Soluble forms of heavy metals in soil were extracted with aqueous solution of HCl in the concentration of 1 mol · dm^{-3}.

Results and discussion

The quality of composts can be evaluated with an aid of a variety of methods, including analysis of their chemical composition, or their influence on the growth and development of plants or soil properties [13]. In the municipal waste composts analyzed in our tests, the total content of heavy metals in the original material was variable. It contained less than ten-fold more zinc and less than a hundred-fold more manganese than copper (Table 1). The references cite that the content of these elements in composts is changeable, a conclusion which is confirmed, for example, by the results reported by Sanchez et al [14], who demonstrated that municipal waste composts contained much more zinc than manganese or copper, whereas Gautman et al [15] proved that composts had more manganese than zinc or copper.

Table 1

Content of copper, zinc and manganese in composts, farmyard manure and soil prior to the experiment [mg · kg^{-1} d.m.]

Metal	Ageing of composts			Municipal solid waste compost	Farmyard manure (FYM)	Soil
	1 month	3 months	6 months			
Cu	161.10	177.45	187.70	67.90	30.10	6.62
Zn	1041.20	1340.60	1031.35	649.55	198.90	31.92
Mn	618.60	796.60	580.70	447.10	443.10	268.10

The length of time during which composts aged in heaps evidently had some influence on the content of each of the tested elements. The highest concentrations of zinc and manganese were found in three-month compost. Further maturation of compost in a heap resulted in a decrease in the content of the elements down to the levels determined in one-month composts. In general, composting causes an increase in the content of heavy metals in the final product. This relationship, however, has not been confirmed in the authors' own study, which may be explained by the fact that the composts used for our analyses were sampled on the same day but they aged in heaps for different periods of time. Thus, the initial material from which the composts were made was characterized by similar albeit not identical properties.

In respect of copper, the concentrations of this metal increased gradually until the sixth month of ageing. The fact that concentrations of heavy metals increasing during the composting process has been demonstrated by other authors [16–17]. Niedzwiecki et al [18] found that composts made from a selected fraction of municipal waste contained more zinc and copper but less manganese compared with the results obtained in our study. Urban green waste contained nearly three-fold less copper than municipal waste composts, and two-fold more versus farmyard manure. Similar relations were discovered for zinc. The content of manganese in this compost was 30 to 78 % lower than in municipal waste composts and close to the content determined in FYM.

The content of heavy metals in soil fertilized with composts depended on the type of applied composts, doses and the time which elapsed from their application.

In the first year after the application of composts, their significant influence on an increase in the total and soluble form of copper content appeared. It was found out that the total content of copper in soil rose as more mature composts had been applied, which was a consequence of the initial composition of composts (Table 2).

Soil fertilized with urban green waste compost contained significantly less copper compared with soil fertilized with an identical dose of municipal waste composts. In the FYM fertilized treatments, much lower concentrations of copper were determined than in soil fertilized with municipal waste composts, but close to the amounts determined in soil amended with urban green waste compost. The highest increase in the soluble form of copper was determined in soil fertilized with one-month compost. Additional mineral fertilization applied alongside the composts created a tendency towards increasing the content of soluble copper in comparison with the treatments enriched with composts alone, applied in identical doses. In the treatments receiving urban green waste compost and FYM, the content of soluble copper in soil was much lower than in the treatments which were fertilized with municipal waste composts.

The direct effect of composts caused an increase in the total and soluble form of zinc in soil. This dependence appeared in all the treatments, which were amended with composts of different age. The content of both forms of zinc was the highest in the soil fertilized with three-month compost. In the soil enriched with urban waste compost and FYM, the respective values were much lower, and within the doses of FYM they were approximately the same.

Table 2

Total contents of copper, zinc and manganese and their soluble forms in the first year after application of composts

No.	Dose $[g \cdot kg^{-1}$ soil]	Cu		Zn		Mn	
		Metal content $[mg \cdot kg^{-1}$ d.m.]					
		total	soluble form	total	soluble form	total	soluble form
1	0	6.58	4.09	31.56	15.81	267.3	168.3
Municipal solid waste compost heap-stored for 1 month							
2	10	8.19	4.50	41.72	22.13	274.0	167.1
3	20	9.80	4.90	51.91	26.52	280.1	168.1
4	30	11.40	5.44	62.31	31.30	286.4	166.1
5	10 + NPK	8.19	4.53	41.50	22.01	273.9	175.0
6	FYM$_N$*	6.86	3.77	33.33	16.71	271.8	167.7
7	FYM$_N$* + NPK	6.85	3.79	33.16	16.40	271.7	174.7
8	FYM$_C$*	7.04	3.94	34.47	16.92	274.5	167.4
Municipal solid waste compost heap-stored for 3 months							
9	10	8.35	4.12	44.79	22.73	275.7	160.7
10	20	10.13	4.42	58.08	28.59	283.7	164.5
11	30	11.88	5.06	71.35	33.64	291.7	160.7
12	10 + NPK	8.34	4.25	44.52	22.73	275.6	168.1
13	FYM$_N$*	6.96	3.83	33.96	17.35	273.3	169.7
14	FYM$_N$* + NPK	6.95	3.85	33.80	17.23	273.2	173.5
15	FYM$_C$*	7.01	3.87	34.28	17.84	274.0	164.4
Municipal solid waste compost heap-stored for 6 months							
16	10	8.46	4.01	41.77	20.59	273.6	156.5
17	20	10.32	4.51	52.00	24.54	279.4	156.7
18	30	12.19	5.07	62.26	28.68	285.2	148.6
19	10 + NPK	8.44	4.14	41.77	21.30	273.4	160.5
20	FYM$_N$*	7.00	3.85	34.23	17.20	273.8	167.0
21	FYM$_N$* + NPK	6.99	3.87	34.01	17.67	273.7	172.9
22	FYM$_C$*	6.98	3.83	34.10	17.87	273.6	164.9
Green waste compost							
23	10	7.25	3.77	37.92	19.34	272.2	158.7
LSD$_{0.05}$							
Dose (d)		1.08	0.69	4.12	4.08	6.57	7.1
Ageing of compost (a)		1.11	0.49	3.98	2.78	4.17	3.2
Interaction: d · a		2.15	0.37	7.29	8.11	13.12	4.2

* Explanation in section Material and methods.

Fertilization with rising doses of municipal waste composts contributed to a gradual increase in the content of manganese in soil. Among the three analyzed metals, manganese was the dominant element in soil. A higher total content of manganese in soil was observed in the treatments with three-month compost than in the ones amended with one- or six-month ones. No significant differences were found between the total content of this element in soil fertilized with composts made from municipal waste versus the ones receiving urban green waste composts and FYM.

With respect to the soluble form of manganese, it was demonstrated that its content increased up to the second dose of municipal waste composts. In the treatments fertilized with FYM, higher quantities of soluble manganese in soil were determined than in soil fertilized with municipal waste and urban green waste composts.

Once the experiment was terminated, that is three years after using the composts, the content of total copper, zinc and manganese slightly decreased, which was caused by the removal of these elements with the yields of the test crops (Table 3). The effect of the type of applied composts as well as their doses was similar to their direct effect. However, these relationships were shaped differently for the soluble forms of the analyzed heavy metals. The content of the soluble form of copper in soil fertilized with one-month compost was higher than in the first year, whereas in soil amended with three- and six-month composts, it decreased.

In respect of the soluble form of copper, such a tendency may have been caused by a larger drop in the soil reaction value in the treatments with one-month compost compared with the ones fertilized with more mature composts. Concerning zinc, higher concentrations of the soluble form of this element were found in soil fertilized with composts which aged for 3 and 6 months than in soil receiving one-month compost. The tendency for an increase in the soluble form of zinc was also noticed in soil fertilized with FYM. The content of soluble manganese in soil enriched with three- and six-month composts decreased in comparison with the first year of the experiment but rose in soil fertilized with one-month compost, especially with its higher doses.

The results of our experiment coincide with the reports presented by other authors. Gigliotti et al [19] demonstrated that as a result of soil fertilization with municipal waste composts, a significant increase in the content of copper and zinc in soil was observed. Similar conclusions were drawn by Jordao et al [20], who claim that application of composts made from municipal waste raise the amounts of available forms of heavy metals in soil. In respect of copper, this increase was proportional to the introduced dose of compost, whereas the content of manganese declined. Petruzzelli et al [21] concluded that the content of heavy metals in soil depended on the applied extractant and changed in time. The highest amounts of soluble forms of copper and zinc were found after soil extraction with *diethylene triamine pentaacetic acid* (DTPA). In their experiment, Bowszys et al [22] demonstrated that application of composts from sewage sludge, in comparison with soil fertilized with farmyard manure, raised the pool of available forms of copper and zinc in soil, a result that occurred in the fourth year after the application of these soil-amending substances. It was also proven that soil analyzed after the termination of the experiment, ie after four years, contained more soluble forms of metals than the soil analyzed at the beginning of the tests.

Table 3

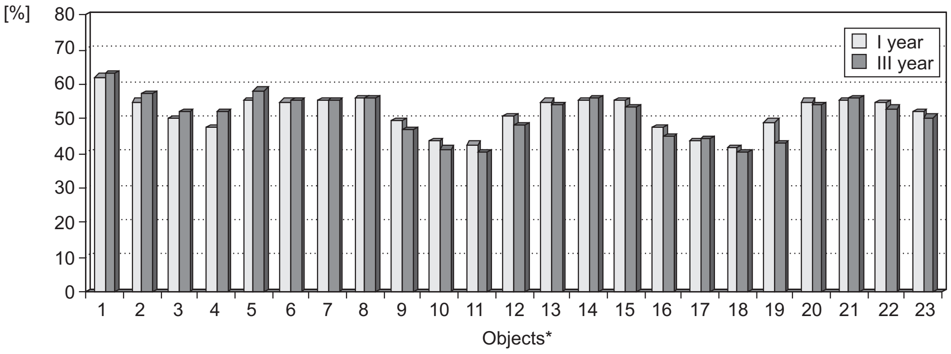
Total content of copper, zinc and manganese and their soluble form in the third year after application of composts

No.	Dose [g · kg^{-1} soil]	Cu		Zn		Mn	
		Metal content [mg · kg^{-1} d.m.]					
		total	soluble form	total	soluble form	total	soluble form
1	0	6.42	4.05	31.22	16.88	265.2	160.5
Municipal solid waste compost heap-stored for 1 month							
2	10	8.01	4.59	41.40	20.42	270.2	157.3
3	20	9.65	5.03	51.41	24.22	274.3	170.4
4	30	11.22	5.83	61.94	28.56	281.7	171.2
5	10 + NPK	8.01	4.67	41.08	19.50	265.3	163.8
6	FYM$_N$*	6.64	3.66	32.71	17.03	268.4	166.9
7	FYM$_N$* + NPK	6.66	3.69	32.67	17.74	268.1	172.0
8	FYM$_C$*	6.89	3.86	34.01	17.53	270.8	163.1
Municipal solid waste compost heap-stored for 3 months							
9	10	8.22	3.86	44.41	23.42	273.2	154.2
10	20	9.89	4.09	57.64	30.07	280.1	156.9
11	30	11.56	4.68	70.82	34.71	287.2	155.4
12	10 + NPK	8.20	3.96	43.19	23.37	273.1	158.7
13	FYM$_N$*	6.78	3.67	33.41	17.78	271.9	167.0
14	FYM$_N$* + NPK	6.71	3.77	33.25	18.01	272.1	171.7
15	FYM$_C$*	6.74	3.58	33.30	17.37	272.5	165.6
Municipal solid waste compost heap-stored for 6 months							
16	10	8.34	3.76	41.35	22.81	272.3	147.4
17	20	10.04	4.43	51.38	26.82	278.7	144.1
18	30	12.00	4.81	61.76	32.30	281.1	142.6
19	10 + NPK	8.29	3.58	41.09	23.12	268.1	153.4
20	FYM$_N$*	6.71	3.64	33.61	17.11	269.3	162.0
21	FYM$_N$* + NPK	6.76	3.79	33.53	17.83	268.7	167.7
22	FYM$_C$*	6.72	3.56	33.54	17.60	270.2	165.1
Green waste compost							
23	10	7.01	3.53	37.38	19.87	269.3	148.5
LSD$_{0.05}$							
Dose (d)		0.92	0.47	3.92	3.12	4.29	4.11
Ageing of compost (a)		1.11	0.63	3.12	3.07	2.19	3.07
Interaction: d · a		2.31	0.67	6.33	7.42	10.05	3.23

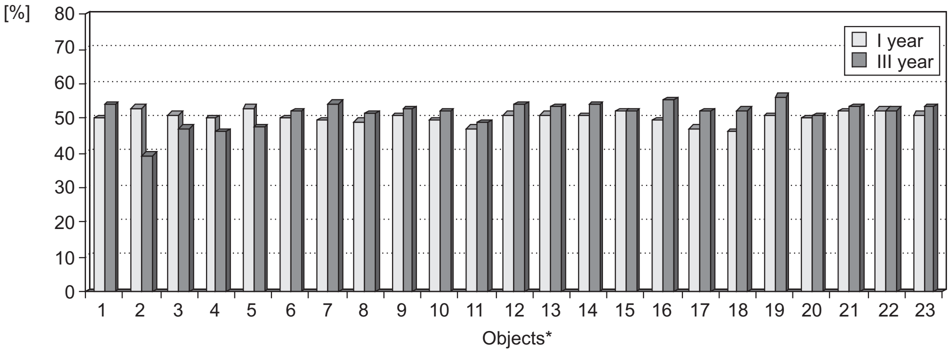
* Explanation in section Material and methods.

In the present research, the percentage of soluble forms of copper, zinc and manganese to the total concentrations of these elements was variable and largely dependent on the factors which shaped their content in soil (Fig. 1).

a) Copper



b) Zinc



c) Manganese

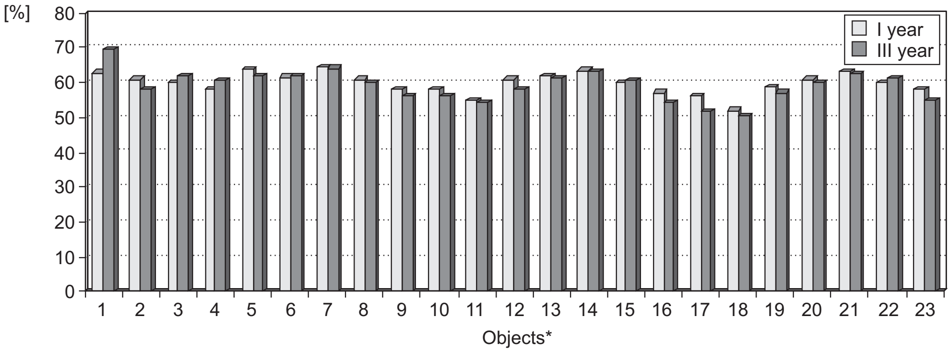


Fig. 1. Share of soluble forms of copper, zinc and manganese in their total concentrations; *1–23 explanations see Table 2

The share of the soluble form of copper to its total content in the first year of the experiment, as shaped under the influence of composts, decreased relative to the control. This value, however, was lower when more mature composts were used. The effect of growing doses of composts on the above parameter was reversely proportional. When higher doses of composts were applied, the ratio of soluble copper to its total content decreased. In the treatments fertilized with farmyard manure, the percentage of soluble copper was higher than in compost-treated soil. In the aftereffect, ie in the third year of the experiment, the effect of higher doses of composts was analogous to their effect in the first year. However, it was noted that the percentage of soluble copper in the total content of this element relative to the first year increased in soil from the treatments fertilized with one-month compost but decreased in soil treated with three- and six-month composts. The same relationship was observed in soil from the pots fertilized with FYM.

The influence of rising doses of composts on the soluble form of zinc relative to its total content was similar to that observed for copper. Nonetheless, such relationships were recorded only as a result of the direct effect produced by composts. The aftereffect was completely opposite. A decrease in soluble zinc in soil in response to the increasing rates of a fertilizer was recorded in the treatments receiving three-month compost. In soil amended with one-month compost, the lowest ratio of this form of zinc to its total content was found when the rate of 20 $g \cdot kg^{-1}$ of soil had been applied, but in soil enriched with six-month compost, the same result was caused by the lowest dose of the fertilizer. The aftereffect of the age of composts became most visible in the case of soil fertilized with the youngest compost, where the ratio of soluble zinc to its total content was much more depressed compared with the results obtained two years earlier.

The application of composts which aged for 3 and 6 months raised the share of soluble zinc in its total content. Such relationships were also demonstrated for the treatments fertilized with FYM, dosed according to the amount of organic carbon as well as total nitrogen. In addition, fertilization with municipal waste and urban green waste composts had some influence on changes in the ratio of soluble manganese to its total soil content. In the direct effect, soil from the treatments fertilized with one-month compost had the highest percentage of soluble manganese. More mature composts, ie three- and six-month old ones, caused a decrease in this parameter. Moreover, as higher doses of these composts were introduced to soil, the ratio of soluble manganese to total manganese decreased. In the treatments fertilized with FYM, solubility of manganese was higher than in the treatments amended with municipal waste or urban green waste composts. In the aftereffect, composts and FYM tended to depress the solubility of manganese in soil.

Some researchers [23] claim that application of municipal waste composts causes a rise in the reaction of soil, but this effect is short-lasting. Such a tendency appeared in our study, as well (Table 4).

In the first year after the application of municipal solid waste and urban green waste composts, the value of pH was much higher than the soil reaction noted as an aftereffect of the fertilizers, that is three years after the application of composts. This change in the

Table 4

Soil reaction value after first and third year of experiment

No.	Dose [g · kg^{-1} soil]	First year		Third year	
		pH (H_2O)	pH (1 mol KCl · dm^{-3})	pH (H_2O)	pH (1 mol KCl · dm^{-3})
1	0	6.96	6.69	6.05	5.43
Municipal solid waste compost heap-stored for 1 month					
2	10	7.40	7.21	6.38	5.69
3	20	7.44	7.19	6.42	5.73
4	30	7.27	7.31	6.47	5.89
5	10 + NPK	7.35	7.17	6.19	5.55
6	FYM_N*	7.35	7.16	6.22	5.44
7	FYM_N* + NPK	7.31	7.14	6.12	5.40
8	FYM_C*	7.23	7.02	6.20	5.59
Municipal solid waste compost heap-stored for 3 months					
9	10	7.29	7.07	6.43	5.97
10	20	7.46	7.18	6.55	6.13
11	30	7.47	7.43	6.60	6.41
12	10 + NPK	7.25	7.02	6.33	5.96
13	FYM_N*	7.39	7.18	6.20	5.37
14	FYM_N* + NPK	7.20	7.15	6.18	5.33
15	FYM_C*	7.42	7.09	6.30	5.41
Municipal solid waste compost heap-stored for 6 months					
16	10	7.00	6.95	6.28	5.61
17	20	7.33	7.15	6.31	5.69
18	30	7.35	7.23	6.39	5.80
19	10 + NPK	6.96	6.90	6.20	5.55
20	FYM_N*	7.37	7.02	6.18	5.32
21	FYM_N* + NPK	7.30	7.00	6.17	5.30
22	FYM_C*	7.38	7.13	6.22	5.43
Green waste compost					
23	10	7.31	7.11	6.33	6.01

* Explanation in section Material and methods.

soil pH may have had some influence on an increase in the amount of soluble forms of the metals in the third year after the application of composts.

Conclusions

1. Fertilization with municipal solid waste composts raised the total content of copper, zinc and manganese in soil. It also affected contents of soluble forms of these

metals. The total content of the metals three years after the application of composts was depressed due to their uptake by the test crops, but the concentration of their soluble forms increased, which may have been caused by a decrease in the soil reaction.

2. The total content of copper in soil fertilized with composts tended to increase as higher rates of the fertilizers were used, a tendency which appeared both as a direct and aftereffect. Among the analyzed composts, the highest increase in the total content of copper was caused by the application of six-month compost. Higher rates of composts led to a depressed share of soluble form of this element in its total content.

3. The highest increase in the total form of zinc in soil occurred after the application of compost which aged in a heap for three months. In the direct effect of composts, the ratio of soluble zinc to its total content was the highest in the treatments fertilized with one-month compost, but in the aftereffect, six-month compost produced an analogous result.

4. Much higher total contents of manganese were found in soil fertilized with three-month compost compared with soil amended with one- and six-month composts. The ratio of soluble form of this element to its total content decreased as more mature composts were used and when higher doses of composts were applied.

5. In soil enriched with urban green waste compost, lower levels of heavy metals were determined compared with soil fertilized with six-month compost made from municipal solid waste. However, in this soil an increase in the share of soluble forms of the analyzed metals versus their total content appeared.

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ZAWARTOŚĆ MIEDZI, CYNKU I MANGANU W GLEBIE NAWOŻONEJ KOMPOSTAMI Z ODPADÓW MIEJSKICH

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Abstrakt: W 3-letnim doświadczeniu wazonowym analizowano wpływ kompostów wytworzonych z niesegregowanych odpadów komunalnych i zieleni miejskiej na zawartość całkowitych i rozpuszczalnych form miedzi, cynku i manganu w glebie. Wykorzystane komposty różniły się między sobą stopniem dojrzałości oraz składem chemicznym materiału wyjściowego.

Stwierdzono, że całkowita zawartość miedzi, cynku i manganu w glebie zwiększała się wraz ze wzrostem dawek kompostów wytworzonych z odpadów komunalnych, co zaobserwowano zarówno w działaniu bezpośrednim, jak i następczym. Największy wzrost całkowitej zawartości miedzi uzyskano w glebie nawożonej kompostem z odpadów komunalnych dojrzewającym 6 miesięcy. Wzrost dawki kompostu powodował obniżenie udziału rozpuszczalnej formy tego pierwiastka w stosunku do jego całkowitej zawartości. Największy wzrost zawartości całkowitej formy cynku w glebie nastąpił po zastosowaniu kompostu dojrzewającego w pryzmie przez okres 3 miesięcy. W bezpośrednim działaniu kompostów udział rozpuszczalnego cynku w stosunku do formy całkowitej był największy na obiektach z kompostem miesięcznym, natomiast w działaniu następczym taki efekt miał miejsce na obiektach z kompostem dojrzewającym 6 miesięcy. W przypadku manganu wyraźnie większe zawartości całkowitej formy tego pierwiastka notowano w glebie nawożonej kompostem dojrzewającym 3 miesiące w porównaniu z glebą nawożoną kompostami po 1 i 6 miesiącach dojrzewania. Udział rozpuszczalnej formy manganu w stosunku do jego zawartości całkowitej zmniejszał się wraz z wiekiem zastosowanych kompostów z odpadów komunalnych, jak też i wskutek zwiększania ich dawek.

W glebie nawożonej kompostem z odpadów zieleni miejskiej odnotowano mniejsze zawartości metali ciężkich w porównaniu z glebą nawożoną kompostem z odpadów komunalnych dojrzewającym 6 miesięcy. W glebie tej nastąpił jednak wzrost udziału rozpuszczalnych form analizowanych metali w stosunku do całkowitej ich zawartości.

Słowa kluczowe: kompost z odpadów komunalnych, kompost z zieleni miejskiej, gleba, miedź, cynk, mangan

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CHANGES IN WATER QUALITY OF MELIORATION SYSTEMS IN UPPER NAREW RIVER CATCHMENT

ZMIANY JAKOŚCI WÓD SYSTEMÓW MELIORACYJNYCH W ZLEWNI GÓRNEJ NARWI

Abstract: The study aimed at determining the quality of surface waters from open melioration ditches in upper Narew River catchment depending on their spatial localization. Following melioration objects were selected to study (open ditches): Orlanka, Suprasl-Grodek-Lachy, Trzcianne-Neresl, Suprasl-Fasty, Choroszcz-Konowaly, Zubowo-Ploski, Zabludow-Rudnia. The objects were meliorated in 1976–1985 in a form of open ditches network and complementary drainage. Melioration of green lands consists of the outflow ditches built to drain larger meadow complexes and accelerate the water outflow from the catchment. Most of melioration ditches are localized around agricultural lands (meadows and pastures), then on arable lands and not agriculturally performed areas (peat-bogs). Green lands are situated on peat-muck soils and occupy about 85 % of area. In total, 21 measurement points were set. Analyses were made since January 2005 till December 2007 once a month. Following items were determined in collected samples: N-NH_4^+, N-NO_2^-, N-NO_3^-, P-PO_4^{3-}, S-SO_4^{2-}, Cl^-, specific conductivity, acidity (pH), Ca^{2+}, Mg^{2+}, Na^+, K^+, $Fe^{2+/3+}$ and Zn^{2+} by means of colorimetric, potentiometric, as well as AAS and EAS techniques.

Water quality in melioration ditches appeared to be dependent on the character of irrigated area. Water from melioration ditches in upper Narew River catchment is characterized by I and II, and sometimes III quality class for surface water. A considerable part of organic soils in upper Narew River valley affect the chemical composition of waters from open melioration ditches.

Keywords: melioration systems, water quality, nitrates, mineral components

A tremendous amount of research has been conducted to evaluate the influence of agricultural management on nutrient transport [1–3].

The main goal of melioration consists in technical and agrotechnical operations that improve the soil productivity. It leads to a proper water balance in agricultural, forest, or aquatic ecosystems, which enhances their productivity and provides with economic efficiency of management [4].

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The drainage water – understood as water from drainage and melioration ditches – is at the start of the minerals migration path within a catchment. Such water is supplied mainly by atmospheric precipitations and transports minerals mainly to surface waters, but also to deep and even to deepest waters [5].

The chemical composition of drainage water may vary, because it can be exposed to direct influences of atmospheric and anthropogenic factors that are associated with application of mineral, organic and natural fertilizers in agriculture [5, 6].

The study was aimed at evaluating the quality of surface waters from open melioration ditches in upper Narew River catchment depending on their spatial localization.

Material and methods

Studies upon the surface water quality in open melioration ditches supplying Narew River and its tributaries were carried out in 2005–2007. The following melioration ditches were selected to studies: Orlanka, Suprasl-Grodek-Lachy, Trzcianne-Neresl, Suprasl-Fasty, Choroszcz-Konowaly, Zubowo-Ploski, and Zabludow-Rudnia (Fig. 1).

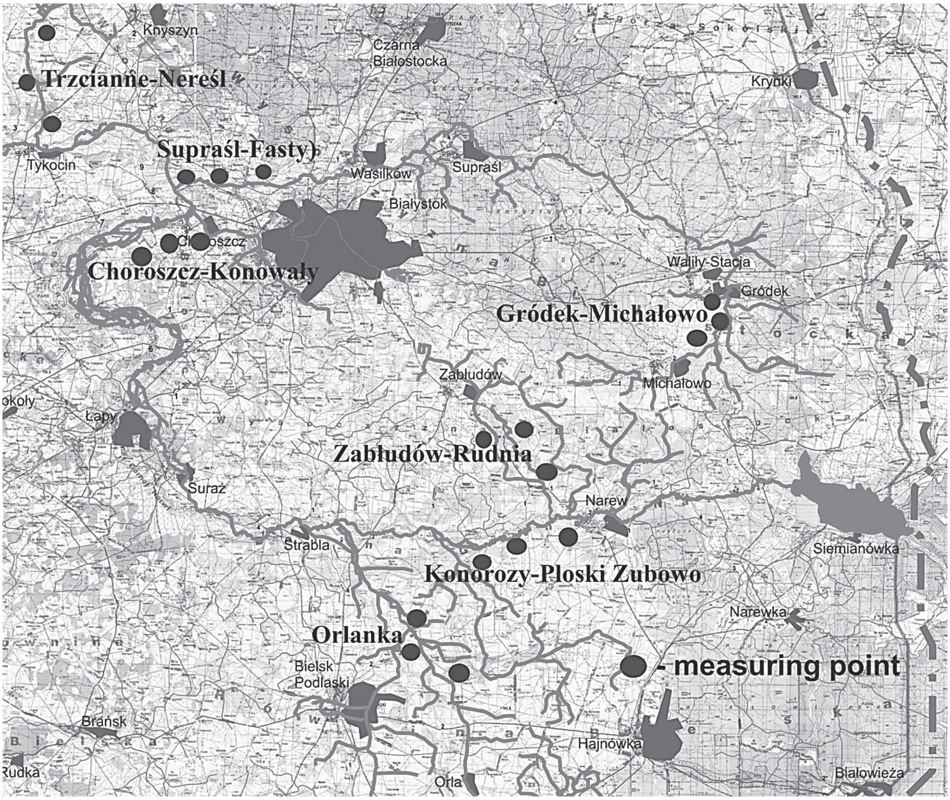

Fig. 1. Localization of sampling points for waters from meliorated areas – upper Narew River

The objects were meliorated in 1976–1985 with a network of open ditches and complementary drainage. Melioration of green lands consists of outflow ditches built to drain larger meadow complexes and accelerate the water outflow from the catchment. Most of melioration ditches are localized around agricultural lands (meadows and pastures), then on arable lands and not agriculturally performed areas (peat-bogs). Green lands are situated on peat-muck soils and occupy about 85 % of area. The thickness of peats was from 0.53 to 2.35 m. Water samples were collected at 3 points from outflow melioration ditches and intensively performed green lands. In total, 21 control points were selected. Analyses were made since January 2005 till December 2007 once a month. Following items were determined in collected samples: N-NH_4^+, N-NO_2^-, N-NO_3^-, P-PO_4^{3-}, S-SO_4^{2-}, Cl^-, specific conductivity, acidity (pH), Ca^{2+}, Mg^{2+}, Na^+, K^+, $Fe^{2+/3+}$ and Zn^{2+} by means of colorimetric, potentiometric, as well as AAS and EAS techniques. The results from determination of the water in studied melioration objects were subject to *Ward Cluster Analysis* (CA).

Results and discussion

The highest mean N-NH_4^+ concentration was found in water of melioration object Suprasl-Grodek-Lachy (2.30 mg · dm^{-3}) (Table 1), which makes it can be classified according to Directive of Minister of Environment (2004) to III quality class of surface waters. The object is localized in majority on areas covered with organic soils with the surplus of peat-muck soils. There are many meadows utilized as pastures, that seem to be the only source of increasing N-NH_4^+ concentration in waters of that object. The melioration works performed in Suprasl River valley made the boggy meadows were transformed into post-bog ones. It seems that elevated N-NH_4^+ concentration may result from the influence of post-bog soils that occur mainly around Suprasl Gorna [7]. The cited study confirm the observations made by Gotkiewicz and Gotkiewicz [8], who reported that meliorated post-bog soils, due to physical and chemical processes, may release considerable amounts of biogenic compounds. Similar N-NH_4^+ concentration in water of meliorated object Suprasl Gorna was recorded by Kiryluk and Wiater [9]. The lowest N-NH_4^+ concentration was reported in water of objects Choroszcz-Konowaly and Orlanka (0.17 and 0.10 mg · dm^{-3}, I quality class for surface water) localized on light soils developed from loamy sands and brown eluted ones. Extreme high concentrations of N-NO_2^- (0.047 · dm^{-3}) and N-NO_3^- (3.8 · dm^{-3}) – III quality class, were recorded in waters of object Choroszcz-Konowaly. Nitrogen compounds release processes from part of organic post-bog soils as well as high level of fertilization applied in those areas, were the probable reasons for that anomaly. The lowest N-NO_3^- concentration (0.6 · dm^{-3}) was determined in object Neresl-Trzcianne localized on sandy soils covered with green lands, which seems to be a natural consequence of such system with sandy soils. Also high level of N-NO_3^- (2.9 · dm^{-3}) was determined in water of melioration object Zabludow. The green lands dominate in these areas and in 85 % they are situated on peat-bog soils. No intensive meadow-pasture management is performed there. Studies conducted by Kiryluk and Skorbilowicz [10] confirm these

Table 1

Physicochemical composition of surface water from open melioration ditches in upper Narew River catchment (mean values for 2005–2007)

Melioration object, soil/indicator, unit	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	$N\text{-}NO_3^-$	$P\text{-}PO_4^{3-}$	$S\text{-}SO_4^{2-}$	Cl^-	EC*	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	$Fe^{2+/3+}$	Zn^{2+}
	[mg · dm^{-3}]						[μS · cm^{-1}]		[mg · dm^{-3}]					
Orlanka *Light loamy sand, meadows and arable lands*	0.10	0.013	1.2	0.27	14	28	540	7.6	120	15	13	7	0.347	0.042
Suprasl Grodek Lachy *Peat-muck, meadows, arable lands, wastelands*	2.30	0.014	1.6	0.14	20	37	573	7.3	91	14	9	5	0.911	0.026
Trzcianne Neresl *Green lands, sandy soils*	0.46	0.011	0.6	0.13	16	20	552	7.8	119	21	17	9	0.810	0.065
Suprasl Fasty *Loose muck and light loamy sands, peats, meadows*	0.50	0.008	1.4	0.07	17	29	571	7.3	121	19	48	28	9.433	1.678
Choroszcz Konowaly *Muck brown eluted soil, grasses*	0.17	0.047	3.8	0.06	30	35	798	7.5	205	25	21	12	0.451	0.074
Zubowo Ploski *Peat-bog, mineral-podzolic, meadows*	0.29	0.010	1.2	0.18	25	26	602	7.4	110	17	16	7	0.421	0.021
Zabludow Rudnia *Mineral podzolic, meadows*	0.38	0.018	2.9	0.22	37	49	663	7.1	131	16	21	13	0.826	0.073

* Electrical conductivity.

results, but they found that nitrate form was characterized by the highest seasonal variability.

The highest calcium concentration was found in water of Choroszcz-Konowaly object ($205 \cdot dm^{-3}$), which ranks it as III quality of surface waters. At the same time, the highest concentration of magnesium ions ($25 \ mg \cdot dm^{-3}$) and the highest value of specific conductivity ($798 \ \mu S \cdot cm^{-1}$) was recorded in that object (II quality class). The soils are intensively fertilized within that area, including liming of strongly acidified ones and it may the main reason for the high levels of macronutrients in waters that flow out of the melioration ditches. Studies performed by Terelak et al [11], Koc et al [12], and Sapek [13] also indicate that. In turn, the lowest levels of macronutrients as well as specific conductivity were recorded in waters flowing out of Suprasl Gorna area (object Suprasl-Grodek-Lachy). As it is known, post-bog and peat areas with meadows and pastures dominate there. The post-bog soils usually contain small amounts of macronutrients, which probably limits their concentrations in waters flowing out of melioration ditches. Studies by Gotkiewicz and Gotkiewicz [8] confirm such observations. These authors also claim that low levels of macronutrients in waters from melioration ditches may be associated with their low concentrations in peat-muck soils.

The pH of the analyzed waters unlikely has no affect on concentration of $S\text{-}SO_4^{2-}$. This follows from the results of studies included in the Table 1. Probably the concentration of $S\text{-}SO_4^{2-}$ in water from drainage ditches is periodically dependent primarily on their water level. Low water levels cause high concentrations of $S\text{-}SO_4^{2-}$ and high water levels – low concentration of $S\text{-}SO_4^{2-}$.

Analysis of results related to water quality in studied melioration objects was made on a base of classification method – Ward Cluster Analysis (CA). Dendrogram (Fig. 2)

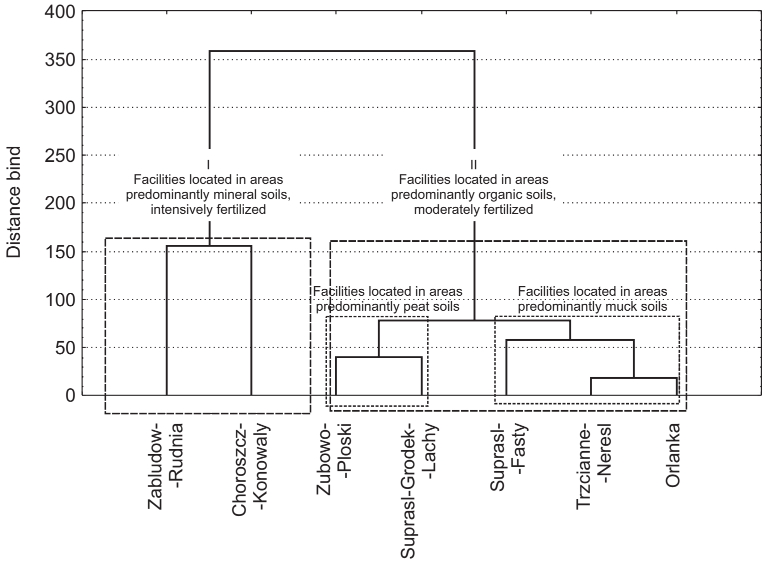

Fig. 2. Ward cluster analysis – waters from melioration systems

presents 2 groups of melioration objects that were arranged due to analysis of generated clusters. One group consists of objects localized on mainly mineral soils that are intensively fertilized and de-acidified, while the other group is composed of objects localized on organic (post-bog and peaty) as well as organic-mineral soils that are less intensively fertilized.

Conclusions

1. The dependence of quality of water in melioration ditches on soil type and land use of drained area was found.
2. Waters from melioration ditches in upper Narew River catchment are characterized by I and II, and sometimes III quality class for surface waters.
3. Majority of organic soils within upper Narew River catchment affect the chemical composition of waters in open melioration ditches.

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Abstrakt: Celem pracy było określenie jakości wód powierzchniowych z otwartych rowów melioracyjnych w zlewni górnej Narwi w zależności od ich lokalizacji przestrzennej. Do badań wybrano następujące obiekty melioracyjne (rowy otwarte): Orlanka, Supraśl-Gródek-Lachy, Trzcianne-Nereśl, Supraśl-Fasty, Choroszcz-

-Konowały, Zubowo-Ploski oraz Zabłudów-Rudnia. Obiekty zostały zmeliorowane w latach 1976–1985 siecią rowów otwartych i drenowaniem uzupełniającym. Melioracje użytków zielonych stanowią rowy odpływowe wykonane w celu odwodnienia większych kompleksów łąk i przyśpieszenia spływu wód ze zlewni. Większość rowów melioracyjnych jest położona w obrębie użytków rolnych (łąk i pastwisk), w mniejszym stopniu na polach ornych oraz terenach nieużytkowanych rolniczo (torfowo-bagiennych). Użytki zielone są położone na glebach torfowo-murszowych stanowiące około 85 % powierzchni. Ogółem wybrano 21 punktów badawczych. Analizy wykonywano w okresie od stycznia 2005 do grudnia 2007 raz w miesiącu. W próbkach oznaczano stężenie $N\text{-}NH_4^+$, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, $P\text{-}PO_4^{3-}$, $S\text{-}SO_4^{2-}$, Cl^-, przewodność właściwą, odczyn (pH), Ca^{2+}, Mg^{2+}, Na^+, K^+, $Fe^{2+/3+}$ i Zn^{2+} metodami kolorymetrycznymi, potencjometrycznymi oraz ASA i ESA.

Na podstawie wyników badań stwierdzono, że jakość wód w rowach melioracyjnych jest uzależniona od charakteru odwadnianego obszaru. Wody z rowów melioracyjnych zlewni górnej Narwi zaliczono do I i II, a czasami III klasy jakości wód powierzchniowych. Znaczny udział gleb organicznych w dolinie górnej Narwi wywiera wpływ na skład chemiczny wód z otwartych rowów melioracyjnych.

Słowa kluczowe: systemy melioracyjne, jakość wód, azotany, składniki mineralne

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EFFECT OF ORGANIC MATTER AND pH ON THE MOBILITY OF SOME HEAVY METALS IN SOILS OF PERMANENT GRASSLANDS IN THE FOOTHILLS OF THE HRUBY JESENIK MTS

WPŁYW MATERII ORGANICZNEJ I pH NA MOBILNOŚĆ NIEKTÓRYCH METALI CIĘŻKICH W GLEBACH TRWAŁYCH UŻYTKÓW ZIELONYCH NA POGÓRZU HRUBÝ JESENÍK

Abstract: In 2008 and 2009 total content of some heavy metals (Zn, Cu, Co, Pb, Cd and Mo) and their water-soluble forms were explored in soils of permanent grasslands of the foothills of the Hruby Jesenik Mts. Relationship between soil reaction and content and quality of organic matter was studied.

The total content of heavy metals ranged from 38.40 to 71.65 mg Zn $\cdot$ kg^{-1}; 10.47–17.46 mg Co $\cdot$ kg^{-1}; 14.30–41.42 mg Cu $\cdot$ kg^{-1}; 3.84–15.53 mg Pb $\cdot$ kg^{-1}; 0.104–0.323 mg Cd $\cdot$ kg^{-1} and 0.129–0.617 mg Mo $\cdot$ kg^{-1}. Content of water-soluble forms ranged from 0.0016 to 1.0100 mg Zn $\cdot$ kg^{-1}; 0.0204–0.2605 mg Co $\cdot$ kg^{-1}; 0.0085–0.2413 mg Cu $\cdot$ kg^{-1}, and 0.0108–0.0485 mg Cd $\cdot$ kg^{-1} of soil. Soil reaction ranged from 4.09 to 5.43 (ie from extremely acid to acid). Results showed that decreasing of pH value caused significant increase of water-soluble fractions of zinc and cobalt content, especially when mineral and organic fertilisers (slurry) were applied. After compost application the inverse relationship water-soluble zinc content and pH was found. Interrelations were not statistically significant in this case.

On permanent grassland soils total organic carbon (TOC) content ranged from 0.60 to 2.55 %. Sum of humic substances (HS) ranged from 4.5 to 8.0 mg $\cdot$ kg^{-1}; with a 1.5–3.3 mg $\cdot$ kg^{-1} and 2.5–5.5 mg $\cdot$ kg^{-1} proportion of humic acids (HA) and fulvic acids (FA), respectively. Humification degree was low (< 20 %). After organic and mineral fertilizers application on permanent grassland soils statistically significant differences were discovered in TOC and HA (compost) content (between the individual rates of organic fertilisers). Because of FA prevailed in humus fractional composition they mostly contributed to the transformation and migration of heavy metals mobile forms. During the experiment with mineral and organic fertilisers the dependence of water-soluble heavy metals and organic matter content was statistically

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significant for cobalt and copper. Cobalt content was inversely proportionate to HA content (r = –0.4021). In a similar way the copper content decreased due to increasing of FA in soils (r = –0.3803).

Keywords: total heavy metals, water-soluble heavy metals, soil reaction, total organic carbon content, humic substances, humic acids, fulvic acids

Soil is the key component of environment and irreplaceable source of most of the biochemical-active heavy metals, which have an effect on man *via* the food chain. As important biogenic elements the heavy metals are on the one hand essential in terms of plant metabolism and on the other hand at high concentrations they may have a toxic effect on the cell and they influence the quality of plant-based products. When studying their bio-accessibility it is of most importance to carry out simultaneous soil monitoring together with monitoring of qualitative and quantitative parameters of soil organic matter and agrochemical soil properties. As the most important component of the soil ecosystem affecting both transport and mobilisation, and mobilisation and local accumulation of soil heavy metals is, in all probability, the soil organic matter. Out of the most important components in the soil was monitored the total content of humus, *humic substances* (HS), particularly the amount of *humic acids* (HA) and *fulvic acids* (FA). These components have an extremely strong effect on the mobility, bio--accessibility and toxicity of the heavy metals [1, 2]. Another very important parameter of soil fertility, which affects the mobility of heavy metals, is the soil reaction [3–7].

Material and methods

In a long-term field trial in the spring and autumn of 2008 and 2009 we took soil samples from *permanent grasslands* (PG) in the locality Rapotin [50°00′12″ N, 17°00′29″ E] (in the foothills of the Hruby Jesenik Mts.) with a view to studying the effect of soil reaction and some parameters of organic matter on the total contents and water-soluble form of heavy metals (Zn, Co, Cu, Pb, Cd and Mo).

Basic soil properties of selected locality are given in Table 1.

Table 1

Characteristics of the locality Rapotin

Altitude a.s.l. [m]	Average temperature [°C]	Annual precipitation [mm]	Soil type	Texture classes [%]			< 0.01 [mm]
				clay	silt	sand	
315–340	7.25	693	Haplic Cambisol	9.4	32.8	57.9	21.4

During the experimental years three experiments, each applying 3 rates of mineral and organic fertilisers, were conducted on the permanent grasslands as shown in Table 2.

The experiment was established in the form of a precise small-plot experiment on experimental plots of 12.5 m^2 each. Apart from the intensity of land use of the PG we monitored burdening of soil with graded rates of fertilisers converted to so-called *livestock units* (LU). All fertilisation treatments were established in 4 replications.

Table 2

Treatments of the experiment with mineral and organic (slurry and compost) fertilization

Treatments of fertilization	Livestock Unit [LU · ha^{-1}]	Dose of nutrition in mineral and organic* fertilizers [kg · ha^{-1}]			Cutting frequency
		N	P	K	
Extensive	0.9	60	30	60	2
Middle intensive	1.4	90	30	60	3
Intensive	2.0	120	30	60	4

* With added fertilization of mineral fertilizers.

Soil samples were taken from a depth of 0.05–0.20 m. Texture was made by the pipette method. In soil soil reaction was determined by the potentiometric method. The total and labile contents of selected trace elements were determined by flame or electrothermal atomic absorption spectrometry after extraction of the soil samples in *aqua regia* (total content) and in the solution of 0.01 M $CaCl_2$ (labile form). *Total carbon content* (TOC) was determined by *oxidimetric titration* [8]. Humic substances (HS) sum, humic acids (HA) sum and fulvic acids (FA) sum were determined by short fractionation method [9]. *Humification degree* (HD) was calculated according to Orlov [10].

The results were assessed using the programme Statistica 7.1 CZ by the method of variance analysis (ANOVA) followed by Fisher's test at a 95 % ($p < 0.05$) and 99 % level of significance ($p < 0.01$).

Results and discussion

The effect of fertilisation on heavy metals content in PG soil was monitored during applying mineral fertilisers, slurry and compost. Total contents of metals corresponded with data given in literature [5].

Table 3

Total content of selected heavy metals in soil [mg · kg^{-1} soil];
values show mean of experiments ± standard error

Treatments of fertilization	Zn	Co	Cu	Pb	Cd	Mo
Extensive	$55.02^a \pm 1.22$	$14.06^a \pm 0.25$	$20.14^a \pm 0.50$	$7.89^a \pm 0.25$	$0.17^a \pm 0.05$	$0.30^a \pm 0.02$
Middle intensive	$53.97^a \pm 1.10$	$13.64^a \pm 0.25$	$20.66^a \pm 0.54$	$8.05^a \pm 0.26$	$0.17^a \pm 0.04$	$0.32^a \pm 0.02$
Intensive	$52.91^a \pm 0.91$	$14.07^a \pm 0.27$	$21.34^a \pm 0.80$	$8.34^a \pm 0.37$	$0.17^a \pm 0.05$	$0.30^a \pm 0.02$

$p < 0.05$ – statistically significant at a 95 %; variants with identical letters express statistically insignificant differences.

Table 3 shows that graded rates of fertilisers gradually increased total contents of Cu and Pb (by 2.6 to 6.0 % relatively and 2.0 to 5.7 % relatively, respectively). Likewise Jezierska-Tys and Frac [11] and Mantovi et al [12] reported that total contents of these metals increased after application of graded rates of fertilisers. However, the application of fertilisers did not significantly ($p < 0.05$) affect their amount in the soil. These findings corresponded with experiments carried out by Erhart et al [13] who discovered that application of compost increased total amounts of Cd, Cu and Pb but not statistically significantly.

Table 4 shows that graded applications of fertilisers increased water-soluble zinc, cobalt and copper content. The highest fertiliser rate (equivalent to 2.0 LU per ha) increased the content of Zn, Co and Cu by 61.2 %, 16.2 % and 19.1 %, respectively.

Table 4

Water-soluble content of selected heavy metals in soil [$mg \cdot kg^{-1}$ soil]; values show mean of experiments ± standard error

Treatments of fertilization	Zn	Co	Cu	Cd
Extensive	0.085 ± 0.007	0.068 ± 0.005	0.068 ± 0.005	0.028 ± 0.001
Middle intensive	0.114 ± 0.014	0.071 ± 0.007	0.068 ± 0.004	0.030 ±0.001
Intensive	0.137 ± 0.031	0.079 ± 0.009	0.081 ± 0.007	0.029 ±0.001

Figure 1 shows that in terms of heavy metals the content of copper increased significantly ($p < 0.05$) in the experiment where slurry was applied. Erhart et al [13] also discovered that compost fertilisation significantly increased the content of copper.

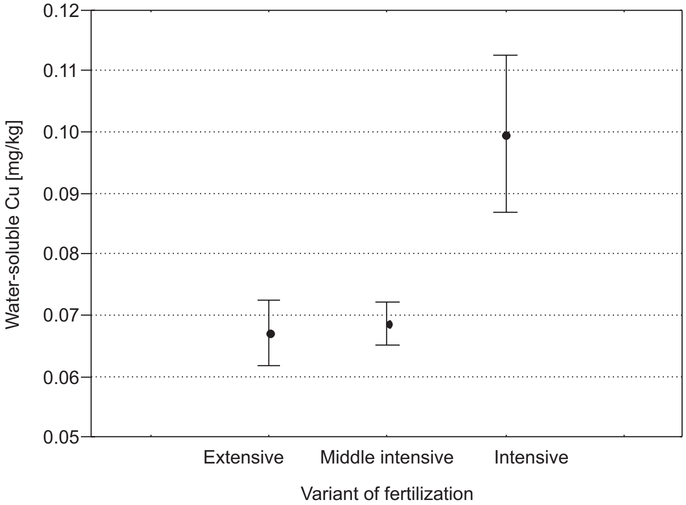

Fig. 1. Effect of fertilization on contents of water-soluble copper [$mg \cdot kg^{-1}$ soil]; errors bars represent Fisher test at $p < 0.05$

During experiments the dependence of water-soluble forms of total elements content was not high. In the slurry-fertilised experiment the most marked statistically highly significant correlation ($p < 0.01$) was found with copper ($r = 0.6311$). The proportion of water-soluble forms of Zn and Co in their total contents increased after the application of fertilisers (Zn from 0.155 % in the extensively loaded treatment to 0.259 % in the intensively loaded treatment and Co from 0.484 to 0.561 %).

During experiments the effect of pH on heavy metals content was also evaluated. Table 5 shows that particularly the water-soluble forms of heavy metals were significantly ($p < 0.05$, $p < 0.01$) dependent on the soil reaction.

Table 5

Effect of pH on the total content and soluble forms of heavy metals in soil

Heavy metals	Mineral fertilization	Compost	Slurry
Total content			
Zn	–0.5212**	0.2033	–0.2058
Co	–0.0324	0.0942	–0.0204
Cu	–0.0556	–0.0236	0.0598
Pb	0.1255	–0.1874	0.3492*
Cd	0.0018	–0.0445	–0.1456
Mo	0.2466	–0.0122	–0.2800
Water-soluble forms			
Zn	–0.5320**	–0.1464	–0.3319*
Co	–0.3628*	0.1822	–0.6253**
Cu	0.2458	0.0037	0.3225
Cd	0.1991	–0.1488	0.1368

* and ** – correlation coefficient significant at the 0.05 level ($p < 0.05$) and 0.01 level ($p < 0.01$), respectively.

The soil reaction affected particularly zinc content. After mineral fertilisers application total zinc content significantly ($p < 0.01$) correlated with pH – see Table 5. Total content of Zn and its soluble forms content increased due to soil acidification. Barancikova and Makovníkova [14] and Chukwuma et al [15] reported similar results. The same trend was monitored in the treatment fertilised with slurry. However a significant dependence ($p < 0.05$) on the soil reaction was discovered only with water-soluble zinc. Mosquera-Losada et al [16] likewise reported a significant effect of fertiliser application on Zn content. Correlation between water-soluble cobalt content and soil acidity was also important. The correlation coefficient $r = –0.6253$ demonstrates the strong effect of pH on water-soluble Co forms.

In Table 6 one may see that in average during experiments a significant ($p < 0.05$**)** effect of fertilisation with organic and mineral fertilisers on the content of C_{ox} was discovered. While in the treatment applying the lowest rate of fertilisers C_{ox} ranged at 1.35 %, the relative amount in the treatment with an intensive level of nutrition was by 12.6 % higher. In terms of the fractional composition of humus one may see a prevalence of fulvic acids (Table 6)**,** which had a predominant effect on the transformation and migration of heavy metals mobile forms.

Table 6

Fractional composition of humic substances in soil;
values show mean of experiments ± standard error

Treatments of fertilization	TOC [%]	HS	HA	FA
		[mg · kg^{-1}]		
Extensive	$1.35^a \pm 0.04$	$6.17^a \pm 0.12$	$2.19^a \pm 0.05$	$3.98^a \pm 0.10$
Middle intensive	$1.37^a \pm 0.03$	$6.20^a \pm 0.11$	$2.25^a \pm 0.05$	$3.90^a \pm 0.09$
Intensive	$1.52^b \pm 0.05$	$6.18^a \pm 0.12$	$2.28^a \pm 0.07$	$3.88^a \pm 0.09$

$p \le 0.05$ – statistical significance at a 95 % level of significance; variants with identical letters express statistically insignificant differences.

The effect of fertilisation on HA content was found to be significant ($p < 0.05$) in the experiment where compost was applied. Based on the rate of compost fertilisation HA content increased from 2.09 (extensive) to 2.45 % (intensive); ie by 17.2 % relatively. Zhang et al [17] also reported that high-quality humus substances (HS) increased due to the application of organic fertilisers.

The sum of humic substances, sum of humic acids and fulvic acids had a significant effect ($p < 0.05$, $p < 0.01$) on the content of water-soluble forms of heavy metals. In the experiment with slurry cobalt content decreased significantly due to HA content ($r = -0.4021$). During experiment with mineral fertilisers a significant correlation was discovered between FA content and the amount of water-soluble copper ($r = -0.3803$), as one may see in Fig. 2.

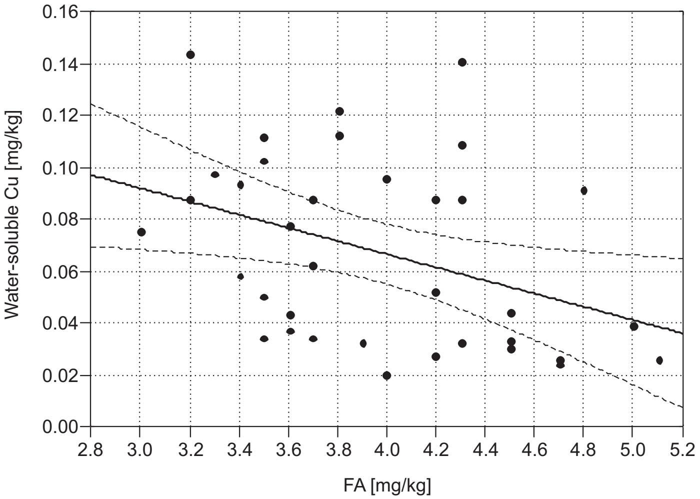

Fig. 2. Correlation between FA content and water-soluble copper [mg · kg^{-1} soil]

After compost amendment no significant ($p < 0.05$) correlation between the organic matter and content of heavy metals was detected.

Conclusions

Graded rates of fertilisers gradually increased the total contents of Cu and Pb but not statistically significantly. A fertiliser rate equivalent to 2.0 LU per ha increased the water-soluble contents of Zn and Co by 61.2 % and 16.2 %, respectively. In slurry-fertilised experiments also significantly increased of Cu by 19.1 % was found. Significantly dependent on soil reaction were particularly heavy metals in water-soluble form, most markedly zinc. Water-soluble Zn content was increasing due the effect soil acidification. Important was the correlation between water-soluble cobalt and soil acidity ($r = 0.6253$). Fertilisation increased TOC content in soil by 12.6 %, relatively. In terms of fractional composition of humus it is evident the prevalence of fulvic acids. During compost application the effect of fertilisation on HA content was significant. After slurry application content of cobalt considerably decreased due to increasing of HA content ($r = -0.4021$).

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WPŁYW MATERII ORGANICZNEJ I pH NA MOBILNOŚĆ NIEKTÓRYCH MIKROSKŁADNIKÓW W GLEBACH TRWAŁYCH UŻYTKÓW ZIELONYCH NA POGÓRZU HRUBÝ JESENÍK

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Abstrakt: W latach 2008–2009 oceniano ogólną zawartość niektórych metali ciężkich (Zn, Cu, Co, Pb, Cd i Mo) oraz ich form wodnorozpuszczalnych w glebach trwałych użytków zielonych Pogórza Hrubý Jeseník. Badano zależności między odczynem gleb i zawartością oraz jakością materii organicznej.

Ogólna zawartość metali ciężkich mieściła się w zakresach: 38,40–71,65 mg Zn $\cdot$ kg^{-1}; 10,47–17,46 mg Co $\cdot$ kg^{-1}; 14,30–41,42 mg Cu $\cdot$ kg^{-1}; 3,84–15,53 mg Pb $\cdot$ kg^{-1}; 0,104–0,323 mg Cd $\cdot$ kg^{-1} i 0,129–0,617 mg Mo $\cdot$ kg^{-1} gleby. Zawartość form wodnorozpuszczalnych wahała się w granicach: 0,0016 to 1,0100 mg Zn $\cdot$ kg^{-1}; 0,0204–0,2605 mg Co $\cdot$ kg^{-1}; 0,0085–0,2413 mg Cu $\cdot$ kg^{-1} i 0,0108–0,0485 mg Cd $\cdot$ kg^{-1} gleby. pH gleb wahało się od 4,09 do 5,43 (tj. odczyn od bardzo kwaśnego do kwaśnego). Wykazano, że obniżenie wartości pH powodowało istotny wzrost zawartości frakcji wodnorozpuszczalnych cynku i kobaltu, zwłaszcza gdy zastosowano nawozy mineralne i organiczne (gnojowicę). Po zastosowaniu kompostu stwierdzono odwrotną zależność między zawartością frakcji wodnorozpuszczalnego cynku i pH. Zależności te nie były istotne statystycznie.

Całkowita zawartość węgla organicznego (TOC) w glebach trwałych użytków zielonych wahała się od 6,0 do 25,5 g $\cdot$ kg^{-1}. Suma substancji humusowych (HS) wahała się od 4,5 do 8,0 mg $\cdot$ kg^{-1}; z udziałem odpowiednio 1,5–3,3 mg $\cdot$ kg^{-1} kwasów huminowych (HA) i 2,5–5,5 mg $\cdot$ kg^{-1} kwasów fulwowych (FA). Stopień humifikacji był niski (< 20%). Po zastosowaniu nawozów organicznych i mineralnych na glebach trwałych użytkach zielonych wykazano statystycznie istotne różnice w zawartości TOC i HA (kompost) (między poszczególnymi dawkami nawozów organicznych). Ponieważ FA przeważają w składzie frakcyjnym próchnicy, najczęściej one biorą udział w przemianach i przemieszczaniu się mobilnych form metali ciężkich. W trakcie doświadczenia z nawozami mineralnymi i organicznymi zależność między zawartością frakcji wodnorozpuszczalnych metali ciężkich i materii organicznej była statystycznie istotna dla kobaltu i miedzi. Zawartość kobaltu była odwrotnie proporcjonalna do zawartości HA ($r = -0,4021$). Podobnie zawartość miedzi obniżała się wraz ze zwiększającą się zawartością FA w glebach ($r = -0,3803$).

Słowa kluczowe: zawartość całkowita metali ciężkich, wodnorozpuszczalne formy metali ciężkich, odczyn gleby, zawartość całkowita węgla organicznego, substancje humusowe, kwasy huminowe, kwasy fulwowe

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FORMATION OF MAIZE YIELD AS A RESULT OF FERTILIZATION WITH ORGANIC MATERIALS

KSZTAŁTOWANIE PLONU KUKURYDZY W EFEKCIE NAWOŻENIA MATERIAŁAMI ORGANICZNYMI

Abstract: The research aimed at determining the influence of organic materials fertilization on the amount of the maize yield. During 2 years of the field study direct and consequent effects of the materials used in fertilizing were determined. The research comprised 7 objects: non-fertilized soil and soil fertilized with mineral fertilizers, cattle manure, compost from green waste, sewage sludge, compost from sewage sludge and straw as well as with a mix of sewage sludge and hard coal ash. Pioneer ‘PR 39F58’ maize cv. harvested for silage was the test plant in both years of the experiment.

Fertilization with organic materials usually resulted in increasing the yield of both fresh matter of the maize top parts and fresh matter of the maize cobs. It was not stated that the examined organic materials affected the yield amount more favorably than mineral fertilizers or manure. From among the analyzed materials, the compost from green waste had the strongest yield-forming effect, whereas the mixture of sewage sludge and hard coal ash had the weakest effect.

Keywords: compost, sewage sludge, organic materials, maize

The presently stated diminution in production of natural fertilizers, and consequently in using those fertilizers in soil fertilization, forces necessity of seeking alternative materials, which could be a source of nutrient elements and organic matter. Emphasized is fertilizing usability of composts from green waste, agri-food industry waste, sewage sludge and composts containing sludge [1, 2]. Used materials, especially sewage sludge, are enriched with various additions (straw, tree leaves, sawdust, bark, peat, brown coal, furnace-ash, calcium oxide) and composted to improve their physical and chemical qualities [1, 3]. Fertilization with organic materials, apart from increasing richness of soil in nutrients and humus, plays a role in limiting deposition of waste.

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Evaluation of organic materials usability in fertilization consists in an analysis of their chemical composition. Moreover, this evaluation focuses on an amount and quality of plants yield as well as on soil properties.

The aim of this research was to determine the impact of the fertilization with selected organic materials on the amount and structure of the maize yield within two years of the field experiment.

Material and methods

The field experiment was set up in 2008 at the Experimental Station of the University of Agriculture in Krakow. The experiment was carried out on Eutric Cambisol containing, on the humus horizon, 25 % of mechanical fraction of diameter below 0.02 mm. The soil properties are shown in Table 1. The heavy metals content in soil and the pH value of soil allowed the fertilization with sewage sludge [4].

The experiment comprised 7 treatments: a non-fertilized soil (A) and a soil fertilized with mineral fertilizers (B), cattle manure (C), compost from green waste (D), sewage sludge (E), compost from sewage sludge and wheat straw (F) as well as with a mixture of sewage sludge and hard coal ash (G). Each treatment was conducted in 4 replications.

Table 1

Selected properties of soil before setting up the experiment

Parameter	Unit	Value
pH_{H_2O}	[-]	6.29
pH_{KCl}		5.40
Hh	[mmol (+) $\cdot$ kg^{-1} d.m.]	18.8
S		126.5
T		145.2
V	[%]	87
$N_{tot.}$	[g $\cdot$ kg^{-1} d.m.]	1.07
$C_{org.}$		9.88
Available P	[mg P_2O_5 $\cdot$ kg^{-1} d.m.]	217.5
Available K	[mg K_2O $\cdot$ kg^{-1} d.m.]	264.1
Cr	[mg $\cdot$ kg^{-1} d.m.]	2.19
Zn		70.7
Pb		26.5
Cu		9.93
Cd		0.55
Ni		5.00
Mn		268
Fe		4 675

Chemical composition of the organic materials used for fertilization is presented in Table 2.

Table 2

Chemical composition of the materials used in fertilization

Parameter	Unit	Material				
		manure	compost from green waste	sewage sludge	compost from sludge and straw	mixture of sludge and ash
Dry matter	[%]	18.5	47.7	35.1	30.8	44.7
$N_{tot.}$	[g · kg^{-1} d.m.]	28.5	14.4	20.2	24.5	14.5
$C_{org.}$		418	202	245	309	152
S		3.46	2.04	10.50	7.30	5.33
P		6.02	1.95	8.22	9.97	6.66
K		13.58	4.47	0.65	4.54	0.75
Mg		4.88	4.70	5.65	6.20	7.55
Ca		11.57	35.88	38.32	31.35	27.38
Na		1.63	0.43	0.17	0.45	0.34
Fe		1.30	6.11	8.75	7.81	8.34
Cr	[mg · kg^{-1} d.m.]	4.31	19.17	17.83	17.93	19.27
Zn		223	285	855	716	520
Pb		5.59	61.33	73.50	59.50	38.73
Cu		23.5	52.8	103.7	99.2	82.8
Cd		1.35	0.88	2.70	2.59	1.48
Ni		4.49	8.59	13.17	11.64	15.43
Mn		141	442	169	198	235

Heavy metals content in all the materials used for fertilization did not exceed acceptable amounts for sludge used in agriculture [4]. The compost used in the experiment was obtained from a container green waste compost facility Barycz, operating under Kneer technology and belonging to Miejskie Przedsiebiorstwo Oczyszczania Sp. z o.o. in Krakow. The sewage sludge (after one year of stabilization) came from a mechanical-biological treatment plant of municipal sewage belonging to Wodociagi i Kanalizacja Krzeszowice Sp. z o.o. The ash from hard coal was obtained from Elektrocieplownia "KRAKOW" S.A. The description of the way of preparing the compost from sludge and straw as well as the mixture of sludge and ash, along with changes in chemical composition of those materials during the composting process, are presented in Tabak's [5] article.

In each year of the experiment the fertilization was carried out before sowing time in spring. In the 1st year of the experiment (2008) the following doses of nutrient elements were used: 160 kg N, 168 kg P_2O_5 and 140 kg $K_2O \cdot ha^{-1}$. Doses of nitrogen and potassium were determined basing on the nutritional requirements of maize, whereas the dose of phosphorus was equalized to the highest dose introduced with one of the organic materials. In the **C-G** treatments the whole nitrogen dose was introduced to the soil in the organic materials used for fertilization. Ammonium nitrate (34 % N), enriched with superphosphate (40 % P_2O_5) and potassium chloride (60 % K_2O) were used to introduce the nutrient elements to the soil of the mineral treatment and also to equalize the doses of phosphorus and potassium in the soils of the remaining treatments. In the 2nd year of the experiment (2009) the following were used: 100 kg N, 30 kg P_2O_5 and 110 kg $K_2O \cdot ha^{-1}$, the fertilization was carried out using the previously mentioned mineral fertilizers.

The Pioneer ‘PR 39F58’ maize cv. was the test plant in both years of the research and it was harvested at the wax maturity stage of the grain, in other words at a proper stage to harvest maize for silage. Thermal and rainfall conditions during the growth period of the maize are presented in Table 3.

Table 3

Mean monthly temperatures and monthly sums of rainfall

Parameter	Year	Month					
		V	VI	VII	VIII	IX	V–IX
Mean temperature [°C]	1st year	13.6	18.4	18.7	18.2	12.6	16.3
	2nd year	13.6	16.0	19.9	18.6	12.9	16.2
Sum of rainfall [mm]	1st year	28.7	26.7	142.6	41.6	98.8	338.4
	2nd year	106.6	122.1	82.7	53.3	61.5	426.2

From 1st May to 30th September mean temperature should be approximately 15 °C [6], which is favorable for proper growth of maize. The mean air temperatures during the period of the experiment were slightly higher and amounted to 16.3 °C in the 1st year of the research and 16.2 °C in the 2nd year. May and September were the cold months in both years of the research. With right distribution, rainfall of 300 mm ensures proper maize development in vegetation season [6]. The amount of rainfall reached the mentioned level in both years. However, the rainfall distribution in the 1st year of the experiment was different than in the 2nd year. A water deficit occurred in May and June in the 1st year (the deficit was replenished in July), whereas in the 2nd year an excess of rainfall occurred in this period.

In the 1st year of conducting the field experiment the maize sowing took place on 9th May 2008, whereas the harvest took place on 4–5th September 2008. In the 2nd year of the experiment the dates were respectively 8th May and 15–16th September 2009. The area of one plot in the experiment was 35 m^2, while the harvest was conducted from an area of 6 m^2. The yield of fresh matter of the maize top parts and the yield of fresh matter of the maize cobs with covering leaves were determined after the harvest. The dry matter content of the maize top parts was determined after drying at 70 °C in a dryer with hot air flow. Values presented in the paper are mean arithmetic values from 4 replications. The results were verified statistically using Statistica 8.0. A univariate analysis of variation was carried out, and the significance of the differences between the mean values for particular fertilizing treatments (within a given year of the experiment or for given total data) was estimated using the Duncan test ($p < 0.05$).

Results and discussion

In the 1st year of the experiment the fertilization with organic materials (except for the sludge and ash mixture) led to an increase in the fresh matter yield of the maize top parts (Table 4).

Table 4

Yield of fresh matter of the maize top parts as well as dry matter content in the top parts

Treatment*	Fresh matter yield of the maize top parts [$Mg \cdot ha^{-1}$]			Dry matter [%]	
	1st year	2nd year	1st year + 2nd year	1st year	2nd year
A	58.87 a**	41.76 a	100.63 a	32.16	31.46
B	98.63 c	59.46 bc	158.09 e	30.96	36.52
C	80.45 b	65.96 c	146.41 d	33.55	37.39
D	75.42 b	63.32 bc	138.74 cd	32.67	38.34
E	80.70 b	63.98 bc	144.68 d	30.83	38.35
F	75.51 b	57.28 b	132.79 bc	30.16	36.04
G	63.93 a	61.00 bc	124.92 b	32.18	37.56

* See “Material and methods”; ** mean values in columns marked with the same letters do not differ statistically significantly at $p < 0.05$, according to the Duncan test.

The effect of the used materials was weaker than of the mineral fertilizers. In the 2nd year of the experiment the organic materials affected the amount of fresh matter yield of the maize similarly to mineral fertilizers (Table 4). It indicates an after-effect of those materials. The highest total yield of fresh matter of the maize top parts was obtained from the mineral treatment, where each type of fertilization produced a statistically significantly higher yield than the yield stated for the non-fertilized object (Table 4). While analyzing the total yield, it was found that the compost from green waste and the sewage sludge affected the yield amount similarly to the manure (hence the most favorably from among the examined organic materials). In compliance with literature data, maize for silage should contain from 28 % to 35 % of dry matter [7]. Such content of dry matter ensures proper course of biochemical processes during silaging. The later the time of harvest, the higher the content of dry matter in plants and the more precise the biomass fragmentation must be (to ensure proper silaging and full eating-up of the silage by animals) [7, 8]. In the 1st year of the experiment the content of the dry matter in top parts of the plants was proper for the maize harvested for silage. In the 2nd year the maize gathered from the fertilized objects was characterized by the content of the dry matter slightly higher than 35% (Table 4).

The influence of the fertilization on the yield amount of the maize cobs fresh matter became apparent in the 2nd year of the experiment (Table 5).

The highest total yield of the cobs fresh matter was obtained from the objects fertilized: minerally, with manure and with the compost from green waste. Yield amount of cobs, more precisely share of cobs in yield of maize top parts, is responsible

Table 5

Fresh matter yield of the maize cobs with covering leaves as well as share of this yield in the fresh matter yield of the top parts

Treatment*	Fresh matter yield of the maize cobs [Mg · ha^{-1}]			Share of the cobs yield in the top parts yield [%]		
	1st year	2nd year	1st year + 2nd year	1st year	2nd year	1st year + 2nd year
A	27.00 ab**	12.48 a	39.49 a	45.89	30.14	39.38
B	32.28 b	22.31 b	54.59 c	32.73	38.06	34.58
C	28.21 ab	21.26 b	49.47 bc	35.05	32.25	33.79
D	27.11 ab	21.85 b	48.96 bc	35.88	34.54	35.30
E	26.12 a	21.30 b	47.42 b	32.27	33.27	32.76
F	26.93 ab	19.67 b	46.60 b	35.60	34.44	35.04
G	23.58 a	20.34 b	43.92 ab	37.15	33.35	35.20

* See "Material and methods"; ** see Table 4.

for energy value of a material. Because degradation (which takes place in the rumen) of starch found in maize grain is slower than degradation of starch from other fodders, the digestive process is stable [8]. What is more, the final degradation of starch takes place thanks to enzymes in the small intestine (obtained glucose is absorbed) – in consequence, feeding with fodder containing starch contributes to diminution of energy deficit which can take place in cattle of high productivity [8]. The share of the cobs yield in the fresh matter yield of maize intended for silaging should amount at least to 30 %, preferably over 40 % (according to some sources even over 50 %) [7, 9]. In the Authors' own research, that share always reached the level of 30 %, however it usually did not exceed 40 % (Table 5).

An increase in yield formation of the maize in the effect of fertilization with organic materials was stated in the Authors' own research (the yield-forming effect of those materials was not stronger than the effect of mineral fertilizers and manure). The analysis of other authors' findings shows that impact of organic materials on yield amount depends on properties of organic materials, soils and plants as well as on conditions for conducting experiments. Literature data indicate both a yield-forming effect of sewage sludge and composts with sewage sludge as well as composts from organic municipal waste [10–13] and lack of a favorable impact of those materials on maize yield amount [14]. Also in the case of other plants, organic materials showed generally a favorable impact on the yield amount [10, 11, 15–18]. In some cases the organic materials revealed a weaker yield-forming effect than mineral fertilization [11, 13], especially in the cases where the consequent effect of the used materials was not analyzed.

A weak yield-forming effect of the organic materials most often results from their inappropriate properties. Using unstable and immature materials (of non-uniform structure, of considerable content of organic matter which is vulnerable to decomposition or materials characterized with a presence of pathogenic microbes) can result in worsening of soil properties (with a change in soil bioactivity, with biological immobilization of nitrogen), and in the effect in the limitation of plants yield formation. Because the biochemical processes during composting of the sewage sludge and the hard coal ash were not advanced [5], it might be the reason of the weak fertilization effect of the sewage and ash mixture. The lack of a significant yield-forming effect of the organic materials can be attributed to too low (compared with alimentary needs of plants) content of nutritional elements in those materials, such as too low potassium content in sewage sludge, or to a small assimilability of those elements [13]. A presence of considerable amounts of heavy metals in the organic materials can also be the reason of the weak yield-forming effect of those materials.

Conclusions

1. Fertilization with the organic materials (compost from green waste, sewage sludge, compost from sewage sludge and wheat straw, mixture of sewage sludge and hard coal ash) usually resulted in increasing the yield of both fresh matter of the maize top parts and fresh matter of the maize cobs.
2. Within two years of the research, the organic materials used in fertilization were not found to have a more favorable effect on the maize yield amount than mineral fertilizers and manure.
3. From among the analyzed materials, the compost from green waste had the strongest yield-forming effect. Fertilization with the mixture of sewage sludge and hard coal ash had the least favorable effect on yield formation of the maize.

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KSZTAŁTOWANIE PLONU KUKURYDZY W EFEKCIE NAWOŻENIA MATERIAŁAMI ORGANICZNYMI

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Abstrakt: Celem badań było określenie wpływu nawożenia materiałami organicznymi na ilość plonu kukurydzy. W dwuletnim doświadczeniu polowym oceniono bezpośrednie oraz następcze działanie zastosowanych do nawożenia materiałów. Doświadczenie obejmowało 7 obiektów: glebę nienawożoną oraz glebę nawożoną nawozami mineralnymi, obornikiem bydlęcym, kompostem z odpadów zielonych, osadem ściekowym, kompostem z osadu ściekowego i słomy oraz mieszaniną osadu ściekowego i popiołu z węgla kamiennego. Rośliną testową w obu latach była kukurydza odmiany 'PR 39F58' firmy Pioneer, zbierana z przeznaczeniem na kiszonkę.

Nawożenie materiałami organicznymi zazwyczaj skutkowało zwiększeniem plonu świeżej masy części nadziemnych oraz świeżej masy kolb kukurydzy. Nie stwierdzono, by badane materiały organiczne oddziaływały na ilość plonu korzystniej niż nawozy mineralne i obornik. Spośród analizowanych materiałów, najsilniejszym działaniem plonotwórczym cechował się kompost z odpadów zielonych, natomiast najsłabszym – mieszanina osadu ściekowego i popiołu z węgla kamiennego.

Słowa kluczowe: kompost, osad ściekowy, materiały organiczne, kukurydza

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INFLUENCE OF LOW RETENTION RESERVOIR ON WATER QUALITY OF SUPRASL RIVER

WPŁYW ZBIORNIKA MAŁEJ RETENCJI NA JAKOŚĆ WÓD RZEKI SUPRAŚL

Abstract: Present research was aimed at evaluating the water quality in small retention reservoir localized within the agricultural catchment in Wasilkow. Three measurement points were selected during the study; their spatial distribution resulted from a possibility to record changes in physicochemical properties of water occurring in analyzed reservoir. Point No. 1 was localized near the inflow, No. 2 in the middle part, No. 3 at the water outflow of the reservoir. Physicochemical analyses of water included following determinations: apparent and real color, turbidity, oxidizability, (specific electrolytic) conductivity, acidity, Kjeldahl's organic nitrogen, ammonia, nitrates(III), nitrates(V), phosphates, total iron, and manganese. Analyses of water samples collected from the surface layer of the littoral were carried out once a month since May 2008 till March 2009. Determinations of water physicochemical parameters were made in accordance with obligatory methods and statistical processing of all achieved data was performed applying two-factorial variance analysis for particular dates and sampling points. Differences were verified using Tukey test.

A prominent seasonality of all examined parameters was observed when analyzing achieved results. Two-factorial variance analysis of mean values of apparent and real color, turbidity, oxidizability, (electrolytic) conductivity, acidity, phosphates, and manganese revealed significant differences between sampling dates, while sampling points had no considerable importance. The Tukey test also verified that significant differences between sampling dates and points were present in the case of nitrates(V), while for nitrates(III) no factor was significant. Only in the case of iron the sampling point appeared to be the most significant, whereas sampling dates were insignificant.

Waters supplying Wasilkow reservoir had more often much lower values of examined physicochemical parameters than those flowing into it, hence the quality of river water below the reservoir became much worse. Observations upon a spatial distribution of studied indicators revealed that reservoir in Wasilkow had no abilities to self-purification.

Keywords: low-retention reservoirs, water pollution, biogenic compounds, water quality

A term "small retention" began to function at the beginning of 70's of the twentieth century [1] and originally was identified with small water reservoirs. They included the

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smallest reservoirs localized along a watershed as well as reservoirs in central part of a catchment. It can be possible, particularly in the case of lowland catchments, because many river fragments, due to riverbed and river valley structure, are appropriate for localizing larger or smaller dam reservoirs. The river dams, resulting from artificial water damming, contribute to intensified sedimentation of substances carried by a river into the retention reservoir. Sometimes, loads are as huge that reservoir's life is only several tens of years. Specificity of retention reservoirs that consists in retaining the nutrients along with their insolation, make them ecosystems susceptible to eutrophication processes. The influence of the reservoir on water quality in a river below the dam is also important [2, 3].

Present research was aimed at evaluating the seasonality of water quality in small retention reservoir in Wasilkow and its influences on physicochemical parameters of river Suprasl water.

Material and methods

Retention reservoir on Suprasl River (from 22+0.400 km to 22+0.800 km of the river course, average flow 9.86 $m^3 \cdot s^{-1}$) localized in Wasilkow was the object of examination. The reservoir surface area is 12 ha, while the area of catchment supplying the reservoir amounts to 1448.2 km^2. Catchment of Suprasl River above the water reservoir Wasilkow is mainly covered with forests, but also agriculturally managed areas. The weir was built in 1968 according to a technical design from 1963 by Central Office for Studies and Designs of Hydrological Engineering "Hydroprojekt" in Warsaw. At first, the reservoir had to serve as a surface water intake point to meet increasing needs of Bialystok citizens and industry, as well as it had to be used as a city bathing place.

Three measurement points were selected during the study; their spatial distribution resulted from a possibility to record changes in physicochemical properties of water occurring in analyzed reservoir. Point No. 1 was localized near the inflow, No. 2 in the middle part, No. 3 at the water outflow of the reservoir. Physicochemical analyses of water included following determinations: apparent and real color, turbidity, oxidizability, (specific electrolytic) conductivity, acidity, Kjeldahl's organic nitrogen, ammonia, nitrates(III), nitrates(V), phosphates, total iron, and manganese. Analyses of water samples collected from the surface layer of the littoral were carried out once a month since May 2008 till March 2009. Determinations of water physicochemical parameters were made in accordance to obligatory methods [4], and statistical processing of all achieved data was performed applying two-factorial variance analysis for particular dates and sampling points. The differences were verified using Tukey test at the significance levels of $\alpha \le 0.05$ and $\alpha \le 0.01$.

Results and discussion

Waters collected in May and June 2008 were characterized by the largest value of color and turbidity, which – according to Woyciechowska and Dojlido [5] – may have resulted from a transitional bottom washout. Another considerable increase of color and turbidity values occurred in February and March 2009, which could be attributed to a supply of organic compounds after snow thawing. Decrease in color intensity was recorded in July 2008 and January 2009. It probably resulted from the oxidation of organic substances. On the base of two-factorial variance analysis of mean color and turbidity values (Table 1), significant differences between sampling dates were confirmed, while values of these indicators depending on the sample collecting points were statistically insignificant. It was observed that the spatial distribution of color and turbidity did not oscillate much, although values of these parameters slightly increased along with the water flowing through the reservoir. In the case of real color, they remained at the level close to inflowing water and water in the reservoir.

Average values of oxidizability depended only on the sampling date. The highest values of the indicator were recorded in January, when samples were collected from beneath the ice cover. It might prove a significant accumulation of organic matter that time. Higher values were found in water flow out of the reservoir rather than at point localized at the water inflow.

Values of (electrolytic) conductivity in waters of studied reservoir were significantly differentiated depending on the sampling dates. Taking into account the dates, mean values of water conductivity oscillated from 266.7 $\mu S \cdot cm^{-3}$ in January 2009 up to 436.7 $\mu S \cdot cm^{-3}$ in August 2008. Moreover, the highest and very similar values of (electrolytic) conductivity were measured in waters collected in June, July, and August 2008, which might be a result of an intensive recreational utilization of the reservoir. Fairly high (electrolytic) conductivity values were recorded in waters collected in September, October, November, and December 2008, which might be the result of intensive autumn rainfalls and associated surface runoffs, as well as possibility of releasing the inorganic substances from bottom sediments. Values of (electrolytic) conductivity for waters were similar at all measurement points.

Water acidity significantly varied depending on sampling dates and oscillated from pH 7.16 to pH 8.17, whereas sampling points had no significant effect. Considerable decrease of pH values at all sampling points was recorded in July 2008 and January 2009, while the highest pH values were found in May and June.

Significant differences (Table 2) in organic nitrogen, ammonia, and nitrates(V) contents in waters of analyzed reservoir in particular sampling dates were proven. The highest mean *total Kjeldahl's nitrogen* (TKN) value was recorded in waters collected in May, June, and August 2008. Another increase of organic nitrogen level was recorded in January 2009. The sampling localization did not affect the TKN contents. The water flow through the reservoir had no influence on lower TKN values, even water flowing out contained more nitrogen than that flowing into the reservoir. It was particularly prominent since September till March. It was probably caused by weekly emptying of the Wasilkow reservoir since September 2008 by Bialystok Water Supply Works. When water was intensively let out, water surface level was much lowered, thus more intensive decomposition of accumulated organic matter occurred on exposed spots of bottom reservoir. Mineral salts and humus substances were the final products of that decomposition. When the reservoir was refilled with water, a secondary water contamination and direct or indirect decrease of the water could take place. Furthermore, exposing large fragments of the bottom often leads to its overgrowing by plants, the

Table 1

Physicochemical properties of "Wasilkow" waters reservoir

Property		2008								2009			Mean B	LSD
		V	VI	VII	VIII	IX	X	XI	XII	I	II	III		
Apparent color [mg Pt · dm^{-3}]	W_{in}	117	57	38	61	38	110	37	75	25	69	69	**63.3**	A = 64.6 B = n.s.
	W_1	93	69	34	63	65	94	35	79	25	91	91	**67.2**	
	W_{out}	86	166	43	53	29	72	44	74	34	81	81	**69.4**	
	mean	**98.7**	**97.3**	**38.3**	**59.0**	**44.0**	**92.0**	**38.7**	**76.0**	**28.0**	**80.3**	**80.3**		
Real color [mg Pt · dm^{-3}]	W_{in}	46	36	37	60	24	55	15	44	10	60	60	**40.6**	A = 14.1 B = n.s.
	W_1	45	37	32	43	24	52	14	43	22	68	68	**40.7**	
	W_{out}	41	34	26	44	25	48	17	52	12	60	60	**38.1**	
	mean	**44.0**	**35.7**	**31.7**	**49.0**	**24.3**	**51.7**	**15.3**	**46.3**	**14.7**	**62.7**	**62.7**		
Turbidity NTU	W_{in}	13.0	10.0	7.0	2.4	1.4	1.4	3.0	3.5	3.4	3.4	3.4	**4.7**	A = 13.5 B = n.s.
	W_1	17.0	10.0	9.0	2.9	1.3	1.3	2.9	3.7	2.6	9.8	9.8	**6.4**	
	W_{out}	16.0	34.0	13.0	1.1	1.4	1.3	3.2	3.5	3.3	3.6	3.6	**7.6**	
	mean	**15.3**	**18.0**	**9.7**	**2.1**	**1.4**	**1.3**	**3.0**	**3.6**	**3.1**	**5.6**	**5.6**		

Table 1 contd.

Property		2008								2009			Mean B	LSD
		V	VI	VII	VIII	IX	X	XI	XII	I	II	III		
COD_{Mn} [mg $O_2 \cdot dm^{-3}$]	W_{in}	3.5	2.5	3.0	3.5	2.5	2.5	1.0	7.0	26.6	7.0	7.5	**6.1**	A = 3.26 B = n.s.
	W_1	3.0	2.5	2.0	5.0	4.5	4.0	0.5	6.0	26.2	7.5	8.0	**6.3**	
	W_{out}	7.0	3.0	5.5	3.5	2.5	1.5	1.5	7.0	25.6	8.5	9.0	**6.8**	
	mean	**4.5**	**2.7**	**3.5**	**4.0**	**3.2**	**2.7**	**1.0**	**6.7**	**26.1**	**7.7**	**8.2**		
Conductivity [$\mu S \cdot cm^{-3}$]	W_{in}	356	408	410	440	383	372	382	371	259	283	283	**358.8**	A = 28.2 B = n.s.
	W_1	409	408	407	434	382	377	380	378	270	292	292	**366.3**	
	W_{out}	358	412	408	436	389	378	387	381	271	290	290	**363.6**	
	mean	**374.3**	**409.3**	**408.3**	**436.7**	**384.7**	**375.7**	**383.0**	**376.7**	**266.7**	**288.3**	**288.3**		
Water acidity pH	W_{in}	7.99	8.18	7.36	7.63	7.67	7.49	7.58	7.50	7.02	7.99	7.99	**7.67**	A = 0.31 B = n.s.
	W_1	7.99	8.19	7.40	7.70	7.73	7.53	7.62	7.44	7.04	8.01	8.01	**7.70**	
	W_{out}	7.97	8.15	7.25	7.49	7.37	7.44	7.59	7.58	7.41	7.93	7.93	**7.65**	
	mean	**7.98**	**8.17**	**7.34**	**7.61**	**7.59**	**7.49**	**7.60**	**7.51**	**7.16**	**7.98**	**7.98**		

LSD (least significant difference) $p \leq 0.5$; Factors: A – times, B – points; n.s. – non-significant; * – $p \leq 0.01$.

Table 2

Physicochemical rates of "Wasilkow" waters reservoir

Property		2008								2009			Mean B	LSD
		V	VI	VII	VIII	IX	X	XI	XII	I	II	III		
TKN [mg TKN · dm^{-3}]	W_{in}	13.3	8.8	1.7	13.3	2.0	1.3	0.4	2.5	6.3	0.4	0.8	**4.5**	A = 6.2 B = n.s.
	W_1	10.4	5.4	2.1	8.8	2.9	0.8	1.3	4.6	7.5	0.4	0.8	**4.0**	
	W_{out}	10.0	4.6	4.2	7.5	8.8	1.7	0.8	5.4	8.8	4.6	5.4	**5.5**	
	mean	**11.3**	**6.3**	**2.6**	**9.9**	**4.6**	**1.3**	**0.8**	**4.2**	**7.5**	**1.8**	**2.4**		
Ammonia [mg N-NH$_4$ · dm^{-3}]	W_{in}	0.22	0.11	0.22	0.18	0.18	0.10	0.18	0.46	0.32	0.34	0.37	**0.24**	A = 0.22* B = n.s.
	W_1	0.29	0.07	0.22	0.21	0.22	0.09	0.15	0.33	0.26	0.34	0.37	**0.23**	
	W_{out}	0.17	0.28	0.21	0.21	0.23	0.29	0.46	0.33	0.34	0.35	0.35	**0.29**	
	mean	**0.23**	**0.15**	**0.21**	**0.20**	**0.21**	**0.16**	**0.26**	**0.37**	**0.30**	**0.35**	**0.36**		
Nitrate(III) [mg N-NO$_2$ · dm^{-3}]	W_{in}	0.046	0.083	0.013	0.003	0.013	0.017	0.066	0.050	0.007	0.297	0.30	**0.057**	A = n.s. B = n.s.
	W_1	0.003	0.040	0.030	0.020	0.003	0.023	0.030	0.056	0.023	0.026	0.026	**0.026**	
	W_{out}	0.050	0.017	0.040	0.020	0.007	0.010	0.066	0.060	0.017	0.010	0.010	**0.028**	
	mean	**0.033**	**0.046**	**0.028**	**0.014**	**0.008**	**0.017**	**0.054**	**0.055**	**0.015**	**0.111**	**0.022**		

Table 2 contd.

Property		2008								2009			Mean B	LSD
		V	VI	VII	VIII	IX	X	XI	XII	I	II	III		
Nitrate(V) [mg N-NO$_3$ · dm^{-3}]	W$_{in}$	1.33	0.44	2.21	1.33	2.21	0.44	2.21	3.10	1.33	3.54	2.21	**1.85**	A = 2.07 B = 0.76
	W$_1$	2.21	0.44	2.21	0.89	1.33	2.21	2.21	4.43	2.21	4.87	4.43	**2.50**	
	W$_{out}$	1.33	0.89	3.54	1.33	2.21	3.54	2.66	5.31	2.66	6.64	4.43	**3.14**	
	mean	**1.62**	**0.59**	**2.66**	**1.18**	**1.92**	**2.07**	**2.36**	**4.28**	**2.07**	**5.02**	**3.69**		
Phosphates [mg PO$_4$ · dm^{-3}]	W$_{in}$	1.30	1.59	1.41	0.59	0.48	0.21	0.55	0.74	0.90	0.58	0.58	**0.81**	A = 0.82 B = n.s.
	W$_1$	1.09	0.82	2.40	0.73	0.47	0.23	0.64	1.35	0.54	0.64	0.64	**0.87**	
	W$_{out}$	1.42	0.88	1.33	0.89	0.59	0.25	0.64	0.70	0.89	0.69	0.69	**0.82**	
	mean	**1.27**	**1.10**	**1.71**	**0.74**	**0.51**	**0.23**	**0.61**	**0.93**	**0.78**	**0.64**	**0.64**		
Iron [mg Fe · dm^{-3}]	W$_{in}$	0.43	0.52	0.41	0.38	0.21	0.38	0.70	0.65	0.70	0.89	0.89	**0.56**	A = n.s. B = 0.32*
	W$_1$	0.43	0.50	0.30	0.34	0.24	0.22	0.68	0.78	0.54	1.03	1.03	**0.55**	
	W$_{out}$	1.05	0.64	0.31	0.32	1.37	1.17	0.76	1.94	0.52	1.01	1.01	**0.92**	
	mean	**0.64**	**0.55**	**0.34**	**0.35**	**0.61**	**0.59**	**0.71**	**1.12**	**0.59**	**0.98**	**0.98**		
Manganese [mg Mn · dm^{-3}]	W$_{in}$	0.081	0.062	0.048	0.026	0.008	0.029	0.163	0.136	0.246	0.147	0.147	**0.099**	A = 0.12 B = n.s.
	W$_1$	0.021	0.063	0.058	0.002	0.007	0.002	0.050	0.218	0.107	0.121	0.121	**0.070**	
	W$_{out}$	0.069	0.040	0.071	0.019	0.135	0.050	0.207	0.124	0.177	0.151	0.151	**0.109**	
	mean	**0.057**	**0.055**	**0.059**	**0.016**	**0.050**	**0.027**	**0.140**	**0.159**	**0.177**	**0.140**	**0.140**		

LSD (least significant difference), $p \leq 0.05$, Factors: A – times, B – points, n.s. – non-significant, * – $p \leq 0.01$.

decaying remains of which during reservoir refilling enhance the negative effects on water quality parameters [6].

Concentration of ammonia in waters was subjected to some extent to seasonality. Mean ammonia levels in waters collected at various dates much differed: from 0.15 mg $N\text{-}NH_4 \cdot dm^{-3}$ in June 2008 to 0.37 mg $N\text{-}NH_4 \cdot dm^{-3}$ in December 2008 (Table 2).

The lowest values of the parameter were observed in April and October 2008, while since May till September 2008 average ammonia concentrations oscillated within the range of 0.15–0.23 mg $N\text{-}NH_4 \cdot dm^{-3}$, and since November 2008 till March 2009, a gradual increase of the item concentration in waters from individual sampling points, was recorded (Table 2). It was probably the effect of emptying the reservoir and thus considerable worsening of water quality. It can be stated that ammonia concentration in waters flowing-out the reservoir was higher than those in flowing-in water. The presence of ammonia in surface waters may be affected mainly by: supplies of that nitrogen form from point and – to a lesser extent – area contamination sources, as well as aerobic conditions and temperature within the reservoir.

Nitrates(III) concentration was high and only slightly differentiated during the survey. A tendency to their elevated amounts in waters collected in May and June as well as November and December, could be observed. The amplitude of nitrates(III) concentrations was narrow (0.003–0.083 mg $N\text{-}NO_2^- \cdot dm^{-3}$); only in February and March 2009, a sudden increase of the parameter up to 0.297 mg $N\text{-}NO_2^- \cdot dm^{-3}$ and 0.30 mg $N\text{-}NO_2^- \cdot dm^{-3}$, respectively, was recorded at the measurement point localized near the water inflow to the reservoir. It could be a consequence of uncontrolled municipal and household wastewaters disposal.

Considering the nitrates(V), a gradual increasing tendency in analyzed waters was observed since December 2008 till March 2009. It should be emphasized that waters flowing-out of the reservoir were characterized by higher concentrations, than at other sampling points, which may suggest the negative influence of the reservoir on Suprasl River waters. Mean values of nitrates(v) percentage in total nitrogen in surface waters exceeding 40 % proved the area contamination [7]. Results referring to nitrates(V) concentration in waters that flew into the reservoir since late autumn and in winter indicated the effect of the area sources of nitrogen origin. Univocal reasons of differences in nitrogen compounds concentrations are hardly recognized. Differences both in uncontrolled surface runoffs, contaminants infiltration from agricultural and suburban areas, and varied weather conditions in particular study months seemed to be the most probable.

Phosphorus compounds are a constant component of surface waters, but their concentrations depend on the level of water contamination, thus they vary during a year [8]. Mean phosphates concentration in examined waters varied depending on the sampling dates, while waters collected from three different points contained similar phosphate levels. Phosphates concentrations in waters supplied to the reservoir indicated their area origin. No influence of the quality of water flowing out of the reservoir on Suprasl River water was observed, because average phosphates concentration within waters in reservoir and those flowing out of it, were similar. In opinion of Kiryluk [9], high phosphates level occurring in May, June, and July 2008 in reservoir water may originate mainly from mineral fertilizers applied for surrounding fields, and river floods during early spring.

Mean iron contents in analyzed waters were not significantly differentiated in reference with the sampling date, yet some increasing tendency was observed in winter. Although amounts of that metal in examined waters much oscillated, tendencies of its higher levels at the water outflow from the reservoir rather than inflow and within the reservoir could be recorded. Elevated amounts of iron may be a cause of its compound precipitation in waters with slightly alkaline reaction, which was present in studied reservoir. According to Gorniak [10], the iron content in surface waters is influenced by a river catchment. Suprasl River is surrounded by organic soils, which favors the release of reduced iron form.

Like in the case of iron, more manganese was found in waters collected in winter. Its elution from a subsoil was a factor determining its concentrations in examined waters. Amount of water-soluble manganese varies very much and usually it is quickly precipitated in a form of colloidal suspension or is bound to bottom sediments and uptaken by plants, which was confirmed by its lower concentrations during the vegetation period.

Natural features of reservoirs and contaminants supplied from their direct catchments affect in concert quite poor water quality, while presence of point sources within a direct catchment determines the water quality regardless of the natural conditions of a reservoir and a catchment [11]. Loading the waters in Wasilkow reservoir with biogens was at relatively low level. The reservoir should be counted to older ecosystems, where matter and principal elements circulation is present, as well as characteristic plant communities developed. These factors should determine the biological balance and appropriate course of water self-purification process. Unfortunately, achieved results not always can confirm it. No doubt, the recreational utilization of the reservoir caused additional increase of majority of measured parameters values in summer. During the study, waters supplying the reservoir were characterized more often by much lower values of analyzed physicochemical indicators than those flowing-out of it. Therefore, quality of the river water below the reservoir was much worsen. Assessment of the water quality if Suprasl River on small retention reservoir in Wasilkow revealed that the reservoir had negative influence on a quality of out-flowing waters, which was probably additionally affected by gradual emptying of examined reservoir. Received results allow to classify water from the first class of water quality to the fifth class waters in accordance with obligatory decree. Parameters lowering the most water quality were: color, turbidity, TKN, COD_{Mn} and nitrate(V).

Conclusions

Summing up the seasonal changes in physicochemical indicators of water quality in studied reservoir, following conclusions may be drawn:

1. Performed analyses of the reservoir water revealed great instability of its quality.
2. Achieved results were considerable variable and depended on seasons.
3. Wasilkow reservoir had no ability to water self-purification, which could have a negative influence on quality of Suprasl River water below the reservoir.

4. No doubt, a gradual emptying the reservoir also had the effect on out-flowing waters quality.

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WPŁYW ZBIORNIKA MAŁEJ RETENCJI NA JAKOŚĆ WÓD RZEKI SUPRAŚL

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Abstrakt: Celem prowadzonych badań była ocena jakości wód małego zbiornika retencyjnego, położonego w zlewni rolniczej w miejscowości Wasilków. Podczas badań wybrano trzy punkty pomiarowo-kontrolne. Wybór i rozmieszczenie punktów badawczych podyktowany był możliwością uchwycenia zmian właściwości fizykochemicznych wody, zachodzących w analizowanym zbiorniku. Pierwszy punkt usytuowany był na dopływie wód, drugi w środkowej części, zaś trzeci na odpływie wody ze zbiornika. Zakres pracy obejmował analizę fizykochemiczną obejmującą następujące oznaczenia: barwa pozorna i rzeczywista, mętność, utlenialność, konduktywność (przewodność elektrolityczną), odczyn oraz zawartości TKN (azotu organicznego metodą Kjeldahla), azotu amonowego, azotanów(III), azotanów(V), fosforanów, żelaza ogólnego i manganu. Badania próbek wody, pobieranych z warstwy powierzchniowej strefy brzegowej, przeprowadzono co miesiąc, w okresie od maja 2008 r. do marca 2009 r. Analizy właściwości fizykochemicznych wody wykonano zgodnie z obowiązującą metodyką, zaś obliczeń statystycznych na podstawie wszystkich uzyskanych wyników badań dokonano, stosując dwuczynnikową analizę wariancji dla poszczególnych miesięcy i punktów pobrania. Różnice oceniono testem Tukey'a.

Analizując uzyskane wyniki badań, stwierdzono wyraźną sezonowość zmienność wszystkich badanych wskaźników. Na podstawie dwuczynnikowej analizy wariancji wartości średnich barwy pozornej, barwy rzeczywistej, mętności, utlenialności, przewodności, odczynu oraz zawartości TKN, azotu amonowego, fosforanów i manganu udowodniono istotne różnice tych parametrów pomiędzy terminami poboru próbek, natomiast punkty ich pobrania nie miały istotnego znaczenia. Testem Tukey'a oceniono również, że istotne różnice wartości ocenianych parametrów pomiędzy terminami i punktami pobrania stwierdzono w przypadku azotanów(V), natomiast w przypadku azotanów(III) żaden z tych czynników nie miał znaczenia. Jedynie w przypadku żelaza istotny okazał się wpływ punktu pobrania, zaś terminy okazały się nieistotne.

Wody zasilające zbiornik „Wasilków" miały najczęściej dużo niższe wartości badanych wskaźników fizykochemicznych, niż wartości wód opuszczających akwen, dlatego też jakość rzeki poniżej zbiornika uległa znacznemu pogorszeniu. Obserwacje przestrzennego rozkładu badanych wskaźników wykazały, że zbiornik w Wasilkowie nie ma zdolności do samooczyszczania.

Słowa kluczowe: zbiornik małej retencji, zanieczyszczenia, związki biogenne, jakość wód

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EFFECT OF COMPOST, BENTONITE AND CaO ON SOME PROPERTIES OF SOIL CONTAMINATED WITH PETROL AND DIESEL OIL

WPŁYW KOMPOSTU, BENTONITU I CaO NA NIEKTÓRE WŁAŚCIWOŚCI GLEBY ZANIECZYSZCZONEJ BENZYNĄ I OLEJEM NAPĘDOWYM

Abstract: The aim of the study has been to determine the effect of compost, bentonite and calcium oxide on the acidity and selected properties of soil contaminated with petrol and diesel oil. Increasing rates of petrol and diesel oil were tested: 0, 2.5, 5 and 10 $cm^3 \cdot kg^{-1}$ of soil. The experiment was carried out in four series: without soil amendments, and with compost (3 %), bentonite (2 % relative to the soil mass) and calcium oxide in a dose corresponding to one full hydrolytic acidity.

Soil contamination with petrol and diesel oil as well as soil amendments had significant effect on the analyzed physicochemical properties of soil. Soil contamination with petrol caused an increase in pH and base saturation as well as a decrease in hydrolytic acidity, sum of exchangeable base cations and base saturation. The effect of diesel oil on the above soil properties was much weaker than that of petrol, although hydrolytic acidity increased while exchangeable base cations, cation exchange capacity and base saturation decreased under the effect of this pollutant. Among the tested soil amending substances, the strongest and most beneficial influence on the analyzed soil properties was produced by bentonite and calcium oxide, especially in respect of hydrolytic acidity. The effect of compost, although generally positive, was weaker than that of bentonite or calcium oxide.

Keywords: contamination, petrol, diesel oil, soil, compost, bentonite, calcium oxide, soil properties

Rapidly developing global economy has led to a considerable increase in consumption of petrochemical products [1, 2]. The dynamic growth of motor transport in Poland, like elsewhere in the world, raises the demand for fuels, and since the fuel resources in our country are more than modest, most oil or gas is imported. This involves such issues as the transport of crude oil over large distances as well as petrol processing, storage and distribution of petrol products, which at any stage can permeate into the environment, including soils [3]. On each occasion, the actual degree of soil contamination depends on the amount of petrol products spilled into soil, the depth of a soil layer

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penetrated with the pollutants and their chemical composition [4] as well as the properties of soil, such as its structure, texture and moisture [5]. Maximum pollution of soil with petroleum products affects mainly the water properties of soil, especially the air and water system. Soil permeability in respect of petrol or diesel oil increases as the water content in soil increases, opposite to the absorption of these substances, which then declines [5]. Petrol and other oil-derived products, when penetrating deeper into soil, clog the spaces through which water and air are transported, as a result of which soil particles turn into lumps and consequently the physical, chemical and biological properties of soil change, leading to a depressed productivity and fertility of soil [6–10]. It is therefore important to search for methods which will reduce the impact of petrol products on soil properties.

Thus, the aim of the present study has been to determine the effect of compost, bentonite and calcium oxide on the acidity and selected properties of soil contaminated with petrol and diesel oil.

Material and methods

A vegetation pot experiment with 4 replicates was conducted in a greenhouse at the University of Warmia and Mazury in Olsztyn (Poland). The experiment was set up on typical brown soil developed from loamy sand, of the following properties: 5.20 pH in 1 mol KCl $\cdot$ dm^{-3}, 27 mmol H^{+} $\cdot$ kg^{-1} hydrolytic acidity, 100 mmol(+) $\cdot$ kg^{-1} *exchangeable base cations* (EBC), 127 mmol(+) $\cdot$ kg^{-1} *cation exchange capacity* (CEC), 78.7 % *base saturation* (BS), 5.5 g $\cdot$ kg^{-1} organic carbon content, and the contents of available phosphorus 21.7 mg $\cdot$ kg^{-1}, potassium 55.5 mg $\cdot$ kg^{-1} and magnesium 32.5 mg $\cdot$ kg^{-1}. Increasing rates of petrol and diesel oil were tested: 0, 2.5, 5 and 10 cm^{3} $\cdot$ kg^{-1} of soil. The experiment was carried out in four series: without soil amendments, and with compost (3 % relative to the soil mass), bentonite (2 %) and calcium oxide (which contains 50 % CaO) in a dose corresponding to one full hydrolytic acidity. Compost was made from leaves (44 %), cattle manure (33 %) and peat (23 %) and matured for 6 months. A detailed specification of the substances added to soil (including the petroleum-based pollutants) was given in Authors previous paper [10]. When the experiment was established, soil in all the pots was enriched with macro- and micronutrients added in the following amounts (per 1 kg of soil): 150 mg N ($CO(NH_2)_2$), 30 mg P (KH_2PO_4), 70 mg K (KH_2PO_4 + KCl), 50 mg Mg ($MgSO_4 \cdot 7H_2O$), 5 mg Mn ($MnCl_2 \cdot 4H_2O$), 5 mg Mo ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) and 0.33 mg B ($H_3BO_3$). The petroleum substances and the other substances analyzed in this research as well as the macro- and micronutrients introduced to soil, all prepared as aqueous solutions, were mixed with 9.5 kg of soil and placed in polyethylene pots. Having prepared the soil, spring barley (*Hordeum vulgare*) Polish cv. ‘Ortega’ was sown in each pot, grown until full maturity and divided into grain, straw and roots. Throughout the whole experiment, the soil moisture was maintained at the level of 60 % of soil capillary capacity. During the harvest of spring barley, soil samples were taken for analyses.

The following were determined in the soil samples: reaction (pH) by potentiometry in aqueous solution of KCl at a concentration of 1 mol · dm^{-3}, hydrolytic acidity (HA) and sum of exchangeable base cations (EBC) using Kappen's method [11]. Based on the hydrolytic acidity (HA) and exchangeable base cations sum (EBC), the cation exchangeable capacity (CEC) and base cations saturation of soil (BS) were calculated from the following formulas: CEC = EBC + HA; BS = EBC · 100 · CEC^{-1}. The results of the tests underwent statistical analysis, which involved a three-factor (1st factor – kind of petroleum substances, 2nd factor – petroleum dose, 3rd factor – kind of neutralizing substance) ANOVA variance test performed with the software package Statistica [12]. Dependences between soil contamination with petrol or diesel oil versus the analyzed soil properties were tested using Pearson's simple correlation coefficients.

Results and discussion

The results of our experiments indicate that soil pollution with petrol and diesel oil, as well as the application of soil amendments such as compost, bentonite and CaO had a significant effect on the reaction of soil cropped with spring barley (Table 1). Soil on which spring barley was grown was characterized by a higher sum of exchangeable base cations, higher cation exchange capacity and higher base saturation in the pots contaminated with petrol than the ones polluted with diesel oil, as opposite to hydrolytic acidity.

Soil contamination with petrol or diesel oil had a significant influence on the analyzed soil properties (Table 1). The value of pH in the series without soil amending substances was positively correlated with the rate of petrol ($r = 0.914$) and, to a small extent, with the rate of diesel oil ($r = 0.200$). In this series, subsequently higher rates of petrol caused a small but successive growth in the pH.

The highest pH was obtained when soil was polluted with 10 cm^3 of petrol per kg of soil. However, in the analogous series involving diesel oil, after spring barley harvest the pollutant was not demonstrated to have produced such an unambiguous effect on soil reaction. The statistical analysis of the results indicate that there is a negative and usually significant correlation between the increasing soil contamination with petrol or diesel oil and the hydrolytic acidity of soil. There was, however, one exception, namely the trials with diesel oil and without soil amendments, where this correlation was positive ($r = 0.704$). As regards diesel oil, the highest hydrolytic acidity was determined in soil polluted with the dose of 10 $cm^3 \cdot kg^{-1}$ of soil. In the analogous series, the increasing rates of petrol caused a successive and significant decrease in hydrolytic acidity of soil ($r = -0.925$).

Introduction of successively increasing rates of petrol and diesel oil led to a significant depression in the sum of exchangeable base cations and cation exchange capacity compared with the control treatments (unpolluted). The lowest value of cation exchange capacity was observed in the pots where the doses of 10 $cm^3 \cdot kg^{-1}$ of soil of either petrol or diesel oil were introduced to soil, in which it was 15 % ($r = -0.946$) and 9 % ($r = -0.936$) lower, respectively, than in the control (unpolluted pots). In this series, the increasing doses of petrol caused a slight increase ($r = 0.900$) in base saturation. In

Table 1

Effect of tested factors on the properties of the soil

Dose of pollutant [cm^3 · kg^{-1} of soil]	Amendments of soil polluted with									
	Petrol					Diesel oil				
	Without additions	Compost	Bentomite	Calcium oxide	Average	Without additions	Compost	Bentomite	Calcium oxide	Average
pH$_{KCl}$										
0	5.62	5.85	6.77	6.48		5.62	5.85	6.77	6.48	
2.5	5.75	6.46	6.89	6.90		5.47	5.97	6.58	6.75	
5	6.00	6.30	7.01	7.02		5.46	5.81	6.66	7.01	
10	6.04	6.15	7.07	6.92		5.63	5.98	6.65	6.80	
r	0.914**	0.248	0.946**	0.661*		0.200	0.440	–0.385	0.582	
Hydrolitic acidity (HA) [mmol H$^+$ · kg^{-1}]										
0	35.6	33.0	19.9	18.4	26.7	35.6	33.0	19.9	18.4	26.7
2.5	32.3	23.3	15.8	16.5	22.0	33.8	31.5	19.1	19.1	25.9
5	28.1	26.6	13.1	12.8	20.2	35.3	34.5	17.3	15.4	25.6
10	27.0	28.5	12.0	14.3	20.5	37.5	31.5	15.0	15.8	24.9
Average	30.8	27.9	15.2	15.5	22.3	35.5	32.6	17.8	17.2	25.8
r	–0.925**	–0.214	–0.910**	–0.730*	–0.783**	0.704*	–0.255	–0.992**	–0.753**	–0.968**
LSD	a – 0.3*, b – 0.4**, c – 0.4*, a · b – 0.6*, a · c – 0.6**, b · c – 0.9**, a · b · c – 1.2**									

Table 1 contd.

Dose of pollutant [$cm^3 \cdot kg^{-1}$ of soil]	Amendments of soil polluted with									
	Petrol					Diesel oil				
	Without additions	Compost	Bentomite	Calcium oxide	Average	Without additions	Compost	Bentomite	Calcium oxide	Average
	Exchangeable base cations (EBC) [$mmol(+) \cdot kg^{-1}$]									
0	78.0	76.0	70.0	74.0	74.5	78.0	76.0	70.0	74.0	74.5
2.5	76.0	84.0	88.0	76.0	81.0	76.0	68.0	78.0	56.0	69.5
5	72.0	78.0	100.0	96.0	86.5	70.0	66.0	60.0	72.0	67.0
10	70.0	68.0	104.0	98.0	85.0	66.0	66.0	68.0	66.0	66.5
Average	74.0	76.5	90.5	86.0	81.8	72.5	69.0	69.0	67.0	69.4
r	–0.962**	–0.694*	0.901**	0.888**	0.792**	–0.975**	–0.779**	–0.343	–0.121	–0.860**
LSD	a – 3.2**, b – 4.6**, c – 4.6*, a · b – 6.5*, a · c – 6.5**, b · c – 9.1**, a · b · c – 12.9**									
	Cation exchange capacity (CEC) [$mmol(+) \cdot kg^{-1}$]									
0	113.6	109.0	89.9	92.4	101.2	113.6	109.0	89.9	92.4	101.2
2.5	108.3	107.3	103.8	92.5	103.0	109.8	99.5	97.1	75.1	95.4
5	100.1	104.6	113.1	108.8	106.7	105.3	100.5	77.3	87.4	92.6
10	97.0	96.5	116.0	112.3	105.5	103.5	97.5	83.0	81.8	91.4
Average	104.8	104.4	105.7	101.5	104.1	108.0	101.6	86.8	84.2	95.2
r	–0.946**	–0.986**	0.899**	0.817**	0.660*	–0.936**	–0.803**	–0.546	–0.238	–0.914**
LSD	a – 3.6**, b – 5.1**, c – 5.1*, a · b – 7.2**, a · c – 7.2**, b · c – 10.2**, a · b · c – 14.5*									

Table 1 contd.

Dose of pollutant [cm^3 · kg^{-1} of soil]	Amendments of soil polluted with									
	Petrol					Diesel oil				
	Without additions	Compost	Bentomite	Calcium oxide	Average	Without additions	Compost	Bentomite	Calcium oxide	Average
Base saturation (BS) [%]										
0	68.7	69.7	77.9	80.1	74.1	68.7	69.7	77.9	80.1	74.1
2.5	70.2	78.3	84.8	82.2	78.9	69.2	68.3	80.3	74.5	73.1
5	71.9	74.6	88.4	88.2	80.8	66.5	65.7	77.7	82.4	73.1
10	72.2	70.5	89.7	87.3	79.9	63.8	67.7	81.9	80.7	73.5
Average	70.7	73.3	85.2	84.4	78.4	67.0	67.9	79.5	79.4	73.4
r	0.900**	–0.180	0.883**	0.756**	0.706*	–0.929**	–0.502	0.691*	0.334	–0.368
LSD	a – 0.7**, b – 1.1**, c – 1.1**, a · b – 1.5**, a · c – 1.5*, b · c – 2.2**, a · b · c – 3.1**									

LSD for: a – kind of petroleum substances, b – petroleum dose, c – kind of neutralizing substance; * and ** – significant at p = 0.05 and p = 0.05, respectively; r – correlation coefficient.

the analogous series with the other petroleum pollutant, a dose of 10 cm^3 of diesel oil per 1 kg of soil led to a decrease in base saturation (r = –0.929) compared with the control.

According to Siuta [13], the soil content of biologically active forms of organic compounds, including petroleum products, affects the dynamics of fluctuations in the oxidation-reduction potential, which largely shapes the changes in the soil environment reaction. The results of our tests on soil pH are supported by the findings cited by Baran et al [14, 15], who studied soils near point pollution sources oozing petroleum-derived products, localized on the grounds of the military airport in Deblin, and found raised pH, sum of exchangable base cations and cation exchange capacity compared with less polluted soils. In another experiment, run by Wyszkowski and Ziolkowska [16], soil contamination with diesel oil depressed soil pH, exchangeable base cations, total cation exchange capacity and base saturation; it also created a tendency for increasing hydrolytic acidity. The influence of petrol on the physicochemical properties of soil was clearly weaker than that of diesel oil.

The soil pH and other properties were obviously affected by the addition of soil amending substances, which allievated the negative effects of soil contamination with petroleum products (Table 1). The soil amendments such as compost, bentonite and CaO significantly influenced soil pH and hydrolytic acidity in pots polluted with petrol or diesel oil. The highest changes were observed after application of bentonite and calcium oxide to soil. In the petrol and diesel oil contained soil, application of the above soil amending substances contributed to a considerable and significant increase in the value of soil pH and to a decrease in hydrolytic acidity as compared with the control series (without any soil amendments). A weaker but positive effect on the hydrolytic activity of soil was produced by compost. Addition of amending substances to soil cropped with spring barley proved to be much more effective in the pots polluted with petrol than the ones contaminated with diesel oil. The mean values of exchangeable cation bases in the series with added soil amending substances were significantly higher than in the series where such substances had not been applied, but only when soil had been contaminated with petrol. In the pots where soil was polluted with diesel oil, bentonite and CaO decreased the cation exchange capacity of soil. The substances added to soil to neutralize the pollutants such as petrol and diesel oil (especially bentonite and CaO) had a positive effect on the base saturation of soil, therefore largely improving this parameter as compared with the control (without soil amending substances).

In the present experiment, introduction of calcium oxide to soil increased soil pH, which confirms the results reported by Czekala [17], Kuziemska and Kalembasa [18] and Wyszkowski and Radziemska [19]. All of these researchers found positive relationships between the soil reaction and application of some organic substances to soil, for example compost or manure. In the authors' own research, reported earlier, it was demonstrated that application of compost to soil polluted with petrol, in contrast to the contaminated one with diesel oil, raised soil pH. Szulc et al [20] claim that composts can improve soil pH. Many authors [13, 16, 18, 19, 21] have demonstrated that calcium oxide introduced to polluted soil decreased its hydrolytic acidity but raised the sum of exchangeable base cations and base saturation, the observations which have been verified by the present study. The effect produced by compost was weaker, but in general positive. Szulc et al [20] as well as Baran et al [15] demonstrated that the sum of exchangeable base cations rose under the influence of compost. The limiting effect of organic matter added to soil, and especially calcium oxide, on hydrolytic acidity, exchangeable base cations and cation exchange capacity has also been evidenced by Wyszkowska [22] and Wyszkowski and Radziemska [23]. The substances mentioned above had a generally positive influence on exchangeable base cations and base saturation, with the application of bentonite and calcium being most effective in pots containing petroleum contaminated soil.

Conclusions

1. Soil contamination with petrol and diesel oil as well as soil amendments had significant effect on the analyzed physicochemical properties of soil.
2. Soil contamination with petrol caused an increase in pH and base saturation as well as a decrease in hydrolytic acidity, sum of exchangeable base cations and base saturation.
3. The effect of diesel oil on the above soil properties was much weaker than that of petrol, although hydrolytic acidity increased while exchangeable base cations, cation exchange capacity and base saturation decreased under the effect of this pollutant.
4. Among the tested soil amending substances, the strongest and most beneficial influence on the analyzed soil properties was produced by bentonite and calcium oxide, especially in respect of hydrolytic acidity. The effect of compost, although generally positive, was weaker than that of bentonite or calcium oxide.

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WPŁYW KOMPOSTU, BENTONITU I CaO NA NIEKTÓRE WŁAŚCIWOŚCI GLEBY ZANIECZYSZCZONEJ BENZYNĄ I OLEJEM NAPĘDOWYM

Katedra Chemii Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Celem badań było określenie wpływu kompostu, bentonitu i tlenku wapnia na kwasowość i wybrane właściwości gleby zanieczyszczonej benzyną i olejem napędowym. Gleba została zanieczyszczona benzyną i olejem napędowym w następujących ilościach: 0, 2,5, 5 i 10 mg · kg^{-1} gleby. Do gleby wprowadzano: kompost i zeolit w ilości 3 % w stosunku do masy gleby oraz tlenek wapnia w ilości równoważnej 1 kwasowości hydrolitycznej (Hh).

Zanieczyszczenie gleby benzyną i olejem napędowym oraz zaaplikowane substancje miały istotny wpływ na badane właściwości fizykochemiczne gleb. Zanieczyszczenie gleby benzyną wywołało wzrost wartości pH i stopnia jej wysycenia kationami o charakterze zasadowym oraz zmniejszenie kwasowości hydrolitycznej, sumy wymiennych kationów zasadowych i całkowitej pojemności wymiennej. Wpływ oleju napędowego na te właściwości był zdecydowanie mniejszy niż benzyny, jednakże zaobserwowano zwiększenie kwasowości hydrolitycznej oraz obniżenie wartości sumy wymiennych kationów zasadowych, całkowitej pojemności wymiennej i stopnia wysycenia gleby kationami o charakterze zasadowym. Spośród zastosowanych substancji neutralizujących najsilniejszym i korzystnym działaniem na badane właściwości gleby odznaczały się bentonit i tlenek wapnia, szczególnie w przypadku kwasowości hydrolitycznej. Wpływ kompostu jakkolwiek na ogół pozytywny był mniejszy niż bentonitu i tlenku wapnia.

Słowa kluczowe: zanieczyszczenie, benzyna, olej napędowy, gleba, kompost, bentonit, tlenek wapnia, właściwości gleby

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Literaturę prosimy zamieszczać wg poniższych przykładów:

[1] Kowalski J. and Malinowski A.: Polish J. Chem. 1990, **40**, 2080–2085.

[2] Nowak S.: Chemia nieorganiczna, WNT, Warszawa 1990.

[3] Bruns I., Sutter K., Neumann D. and Krauss G.-J.: *Glutathione accumulation – a specific response of mosses to heavy metal stress*, [in:] Sulfur Nutrition and Sulfur Assimilation in Higher Plants, P. Haupt (ed.), Bern, Switzerland 2000, 389–391.

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