SOCIETY OF ECOLOGICAL CHEMISTRY AND ENGINEERING

ECOLOGICAL CHEMISTRY AND ENGINEERING A

CHEMIA I INŻYNIERIA EKOLOGICZNA A

Vol. 19 No. 4–5

OPOLE 2012

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Ecological Chemistry and Engineering A / Chemia i Inżynieria Ekologiczna A
is partly financed by Ministry of Science and Higher Education, Warszawa

ISSN 1898–6188

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DOI: 10.2428/ecea.2012.19(04)035 ECOL CHEM ENG A. 2012;19(4-5):341-351

Agata BARTKOWIAK[1]

TOTAL CONTENTS AND AVAILABLE FORMS OF NICKEL IN AGRICULTURAL ALLUVIAL SOILS

ZAWARTOŚĆ FORM CAŁKOWITYCH I PRZYSWAJALNYCH NIKLU W ALUWIALNYCH GLEBACH UPRAWNYCH

Abstract: Alluvial soils located in river valleys constitute a diverse cover, which consists of mineral as well as mineral-organic and organic soils, with very different physicochemical properties. The subject of this study was to determine the nickel content in alluvial soils formed from gyttia of the biogenic plain of the Unislawski Basin. Soil samples were collected from seven soil profiles. Selectd physicochemical properties were determined aplying the methods commonly used in soil science laboratories. In the samples analysed the total nickel content was defined after mineralization in a mixture of acids HF + $HClO_4$ and its easily available DTPA-extracted forms. The content of total and mobile forms was reported using the atomic absorption spectrophotometry method using the PU 9100X spectrometer (Philips). The total content of nickel ranged from 0.6 mg $\cdot$ kg^{-1} to 18.04 mg $\cdot$ kg^{-1}.The highest content of this element was noted in surface and subsurface horizons and the enrichment horizons of organic matter. In the soil samples the total nickel content was similar to the geochemical background level, while the content of mobile forms of this element was lower than the values considered toxic. In the soils analysed the content of DTPA-extractable forms ranged from 0.14 mg $\cdot$ kg^{-1} to 2.09 mg $\cdot$ kg^{-1}.

Keywords: nickel in soil, alluvial soils, total and DTPA-extractable forms

Introduction

A growing interest in microelements resulting from the natural environment pollution calls for the control of the pollution amounts in the air, water and, mostly, in soil, which is obvious since soil is the first link of the food chain, affecting the chemical composition of plant materials determining the human and animal health. Heavy metals are a specific group of pollutions present in soil. This specific nature comes from their character; those are the elements which do not undergo degradation and decomposition, additionally they occur in all the soil types.

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Nickel is a metal which is worth noting in terms of environmental protection. It is not a microelement indispensable for the functioning of living organisms, however, numerous research have shown its presence in the adequate pattern of physiological processes in plants, animals and microorganisms [1–5]. Crops uptake nickel easily, usually proportionally to its concentration in soil, until the level of toxicity is reached. There are, however, differences in the phytoaccumulation and phytotoxicity of nickel depending on its form in soil and on the plant species [6, 7]. The occurrence of that element is connected with the content in the parent rock [8], while the mobility is conditioned by the mineralogical and the granulometric composition of soils [9]. A strong bond with nickel formed by mineral colloids and iron hydroxide limits the mobility of that microelement in the soil environment.

The aim of the present research was to evaluate the total content and the available forms of nickel in alluvial soils formed on gyttias of the biogenic plain of the Unislaw Basin.

Material and methods

The research material involves 7 soil profiles, located in the area of the Unislaw Basin (the Lower Vistula Valley) in the vicinity of Bloto (Fig. 1). The area exposed to the analyses is under agricultural use for the field cultivation of vegetable crops, sugar beet, rape and wheat. The soil material was made up by the carbonate formations, emerged in the stagnant muddy river lakes grown with plants, covered with peat or alluvia, affecting their composition and physicochemical properties.

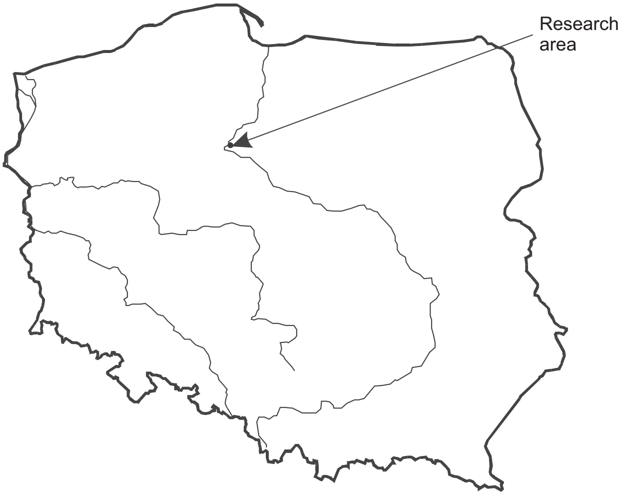

Fig. 1. Research area location

The soils have been classified as Calcari-Mollic Fluvisols, demonstrating high fertility. The soil for laboratory tests was sampled from the morphologically separated layers. The research material was dried and screened through the sieve with the mesh 2 mm in diameter. For the samples prepared in such way, selected physicochemical properties were defined applying the methods commonly used in soil science laboratories. In the samples analysed there was measured the total content of nickel after the mineralization in the mixture of HF + $HClO_4$ acids with the Crock and Severson's method [10] and its easily available forms, extracted with DTPA, according to Lindsay and Norvell [11]. The total contents and mobile forms were determined applying the method of atomic absorption spectroscopy (AAS) with the PU 9100X spectrometer (Philips). To verify the accuracy of the results, the analysis of the certified material SV-M as well as the so-called zero tests were made, which were exposed to the identical analytic procedure as the soil samples. All the assays were made in three repetitions; the paper presents arithmetic means of the results.

Results and discussion

The soils showed a clear variation from most soils in Poland. Next to calcium carbonate, their main component was organic matter. In the earlier reports [12] there was noted the lithologic discontinuity of the soils discussed. The fluctuations in the content of carbonates, organic substance and non-carbonate mineral substance point to the occurrence of many sedimentation cycles in their formation. The characteristic feature of the soil profiles was a high content of carbon carbonate reaching 76.8 %, and organic matter – 355.0 g · kg^{-1} (Table 1). The occurrence of considerable amounts of $CaCO_3$ was observed already in arable and humus horizons (Apca), which, on average, contained 22.0 % of that compound. The analysis of the content of carbonates in respective types of gyttia demonstrated a high variation. Among the gyttias, the lowest amount of carbonates was recorded for claygyttia, while the highest – for lime gyttia. Lime gyttia contained, on average, 63.3 % of $CaCO_3$, at the maximum amounts reaching 76.08 %. Calcium carbonate was also identified in the horizons of low peat, however, those were little amounts, ranging from 4.9 to 6.8 %. Even lower amounts of $CaCO_3$ were noted in the Gleysols in which the content of calcium carbonate did not exceed 4.5 %, at the minimum content of 0.6 %. The analysis of the profile distribution of carbonates showed the occurrence of the highest amounts of that compound in the deepest horizons of the profiles. In the soils investigated the content of organic carbon ranged from 1.4 g · kg^{-1} in the claygyttia horizon to 355.0 g · kg^{-1} in the low peat horizon. The variation in the content of organic carbon was connected with the location of the sampling site in the profile, which is characteristic for multilayer alluvial soils. Definitely highest amounts of C-org. were reported in peat horizons and in the detritus gyttia horizon. Next to the horizons enriched with organic matter, the highest content of organic carbon was noted in the surface horizons. The contents of organic carbon in the profiles analysed decreased with depth. In the soils investigated high amounts of $CaCO_3$ determined the neutral or slightly alkaline reaction of the formations all across the profile. Both the active and exchangeable acidity did not show a considerable variation across the profiles. The active acidity ranged from 7.03 to 7.87 pH units, while exchangeable acidity – from 6.88 to 7.41 (Table 1). All the genetic horizons of the profiles showed a high texture variation, while the grain size composition analysis highlighted the clay nature of the sediments.

Table 1

Selected physicochemical properties of the soils

Profile No.	Horizon	pH		C_{org}	$CaCO_3$	Fraction < 0.002 mm
		H_2O	1 M KCl	[g · kg^{-1}]	[%]	
I	Apca	7.67	7.03	55.8	16.2	48.3
	IICgyica	7.76	7.12	77.3	29.8	70.6
	IICgydca	7.51	6.88	195.2	36.7	n.d.
	IICgyca1	7.86	7.24	30.6	59.5	70.7
	IICgyca2	7.86	7.39	9.5	9.8	61.4
II	Apca	7.59	7.13	63.9	21.8	64.0
	Aaca	7.68	7.15	65.9	27.2	60.3
	IICgyica	7.64	7.17	63.9	40.2	81.5
	IICgyca1	7.59	7.2	24.4	68.4	47.6
	IICgyca2	7.63	7.14	59.8	46.0	78.4
	IICgydca	7.64	7.16	112.9	56.5	n.d.
	IICgyca	7.65	7.2	14.7	51.6	35.5
III	Apca	7.84	7.41	60.9	24.4	40.6
	Aaca	7.57	7.27	65.7	25.6	38.5
	Otnica	7.52	7.14	355.0	6.8	n.d.
	Aaca	7.26	6.96	63.1	5.3	11.3
	Gca	7.61	7.09	65.8	2.4	6.7
	IICgyi	7.68	7.14	7.9	8.5	35.0
	IICgyica	7.75	7.30	9.7	39.8	29.8
IV	Apca	7.60	7.30	59.4	26.5	51.0
	Aacag	7.68	7.27	19.7	6.7	18.3
	Gca1	7.87	7.26	4.9	4.5	32.9
	G2	7.79	7.16	5.3	0.6	31.9
	IICgyigg	7.86	7.41	1.4	12.1	42.0
V	Apca	7.60	7.33	80.3	23.6	60.0
	Aacag	7.53	7.26	78.0	24.9	64.5
	IICgyica	7.53	7.21	65.0	39.1	57.2
	IICgyd1	7.30	7.09	342.8	21.0	n.d.
	IICgyd2	7.60	7.12	257.8	22.8	n.d.
	IICgyd3	7.67	7.4	46.5	48.7	n.d.
	IICgyca	7.57	7.48	14.4	76.1	61.9
VI	Apca	7.38	7.20	50.2	15.9	66.5
	Aaca	7.37	7.30	5.1	69.3	29.3
	IICgyicag	7.37	7.3	29.0	35.2	65.1
	IICgyca	7.42	7.25	2.3	70.1	58.1
	IICgyica1	7.44	7.30	4.1	20.5	23.0
	IICgyica2	7.46	7.31	2.8	40.6	19.4
	IICgyica3	7.46	7.35	2.2	37.5	16.2

Table 1 contd.

Profile No.	Horizon	pH		C_{org}	$CaCO_3$	Fraction < 0.002 mm
		H_2O	1 M KCl	[g · kg^{-1}]	[%]	
VII	Apca	7.23	7.20	64.9	25.0	35.6
	IICgyica1	7.27	7.25	58.3	46.8	31.3
	IICgyica2	7.23	7.20	90.6	34.5	21.9
	Otnica1	7.03	6.99	373.4	4.9	n.d.
	Otnica2	7.17	7.10	312.9	6.2	n.d.
	IICgycagg	7.46	7.30	18.0	65.4	12.2

n.d. – not determined.

The total content of nickel ranged from 0.6 mg · kg^{-1} to 18.04 mg · kg^{-1} (Table 2). Its highest contents were noted in humus horizons (Ap and Aa) and in the horizons enriched with organic matter (detritus gyttia, low peat). Kabata-Pendias and Pendias [8] as well as Ruszkowska and Wojcieska-Wyskupajtys [13] confirm a special capacity for nickel bonding by organic substance. The occurrence of nickel in soils determines mostly its content in the parent rocks of soils and their richness with iron and clay minerals [14]. The occurrence of nickel in soils is connected with the alkaline igneous rocks and with sedimentary clay rocks. Nickel most frequently accompanies rock-forming magnesium-iron silicates [15]. Basing on the present research in the arable soils of the Pomorze and Kujawy Region, Piotrowska and Terelak [16] found that the content of nickel ranged from 5.3 mg · kg^{-1} to 7.2 mg · kg^{-1}, and the average content of that element was 6.3 mg · kg^{-1}. As reported in literature [17–19], the content of Ni in the surface horizons of various soils of the region ranged from 1.1 mg · kg^{-1} to 61.8 mg · kg^{-1}. In the Phaeozems of the Kujawy Region the content of total nickel was between 1.4 mg · kg^{-1} and 61.4 mg · kg^{-1}, while in the typologically varied soils of the Inowroclaw Plain the contents were much lower and ranged from 4.5 mg · kg^{-1} to 23.6 mg · kg^{-1}. Similar contents of the element (12.5; 44.2) mg · kg^{-1} were recorded by Kobierski et al [20] in alluvia within the flood banks of the Unislaw Basin as well as by Wojcikowska-Kapusta and Niemczuk [21] in typologically varied arable soils of the Lublin Upland and in the vicinity of Sandomierz (0.5; 46.5) mg · kg^{-1}. In the soils analyzed the total Ni content was similar to the content of the geochemical background [8] and it did not exceed the admissible concentrations for unpolluted soils [22].

Defining the content of phytoavailable forms of Ni in soils is essential due to its availability by the plants determined by the concentration of mobile forms in soil. It is, in general, uptaken proportionally to its concentration in soil [23], and its toxic effect on the plants is visible in disturbed photosynthesis, transpiration and the process of nitrogen binding. In the soils investigated the contents of the forms extracted with DTPA ranged from 0.14 mg · kg^{-1} to 2.86 mg · kg^{-1} (Table 2). The highest contents of the available nickel were noted, similarly as in the case of total forms, in the horizons enriched with organic matter, which can point to a greater Ni concentration in organic matter, which, in turn, coincides with the results reported by Kabata-Pendias and

Table 2

Total Ni contents and its DTPA-extractable forms

Profile No.	Horizon	Total content	Extractable (DTPA)
		$[mg \cdot kg^{-1}]$	
I	Apca	17.39	1.72
	IICgyica	8.85	1.77
	IICgydca	10.84	2.07
	IICgyca1	5.90	0.58
	IICgyca2	2.66	0.35
II	Apca	12.11	1.31
	Aaca	12.01	1.54
	IICgyica	4.70	0.47
	IICgyca1	3.38	0.76
	IICgyca2	4.73	0.76
	IICgydca	6.09	1.26
	IICgyca	4.39	0.56
III	Apca	12.73	1.43
	Aaca	13.31	1.59
	Otnica	13.91	2.09
	Aaca	6.21	0.67
	Gca	6.09	0.37
	IICgyi	4.98	0.40
	IICgyica	2.29	0.23
IV	Apca	11.86	1.44
	Aacag	5.88	0.74
	Gca1	5.00	0.46
	G2	7.80	0.46
	IICgyigg	1.61	0.40
V	Apca	12.61	1.24
	Aacag	12.96	1.41
	IICgyica	6.80	0.80
	IICgyd1	5.03	1.46
	IICgyd2	9.26	1.96
	IICgyd3	5.03	0.69
	IICgyca	6.34	2.86
VI	Apca	18.04	1.52
	Aaca	3.38	0.46
	IICgyicag	5.70	1.39
	IICgyca	5.30	0.53
	IICgyica1	2.61	0.07
	IICgyica2	2.19	0.28
	IICgyica3	0.66	0.14

Table 2 contd.

Profile No.	Horizon	Total content	Extractable (DTPA)
		[mg · kg^{-1}]	
VII	Apca	10.14	0.56
	IICgyica1	2.89	0.29
	IICgyica2	1.18	0.34
	Otnica1	1.23	0.35
	Otnica2	1.31	0.18
	IICgycagg	10.14	0.56

Pendias [8] showing a high accumulation of nickel in bioliths as well as the occurrence in the soils in the form of bonds with organic matter in a form of mobile chelates. With a low pH, the strength of nickel bond by the organic matter of the soil is low, while in the neutral pH the bond is very strong and it is important in terms of bioavailability [24, 25]. Gebski [26] informs that the mobility of heavy metals increases most probably as a result of the emergence of mobile complexes of heavy metals with organic matter. Such bonds are easily available to plants, which coincides with the reports by Taylor and Olsson [27].

Nickel is considered to be a mobile element. Many authors stress that the availability and the mobility of nickel in soil is affected by very many factors, such as the content of organic matter, the concentration of iron compounds and pH as well as the grain size composition of the soil itself [28–32]. Weng et al [31] claim that the factor determining the mobility of nickel in soil is its reaction, which can be due to the sorption capacity of organic matter of soil towards metals depending strongly on pH [32]. Increased soil acidity enhances the solubility of coordination complexes of nickel in the soil solution and the bioavailability of that element [33]. In the soils of acid reaction its solubility increases considerably, however, its susceptibility to the formation of bonds with organic substance also results in a high mobility of nickel when exposed to neutral or alkaline reaction [8]. Besides, a lower content of organic matter is less important in limiting the bioavailability of nickel, as compared with acid soil [25]. Soil liming is, therefore, a factor limiting the phytoavailability of nickel. In the soil samples investigated there were noted low contents of mobile nickel forms considered to demonstrate non-toxic values, as affected by the neutral or alkaline reaction of the soils (Table 2).

Similarly the soils containing more silt and clay fractions usually show a higher content of that element [34, 35], which is confirmed by the present research in which the statistical analysis identified the correlation between the content of available nickel forms and the content of colloid clay. The highest share of available forms in the total content of the element was noted in most profiles analysed in the horizons of clay and lime gyttia (Fig. 2). Wall [36] reports on a strong dependence between the mechanical composition of soil and the phytoavailability of nickel to plants (buckwheat). The author claims that the lowest concentration of nickel is found in the plants grown in

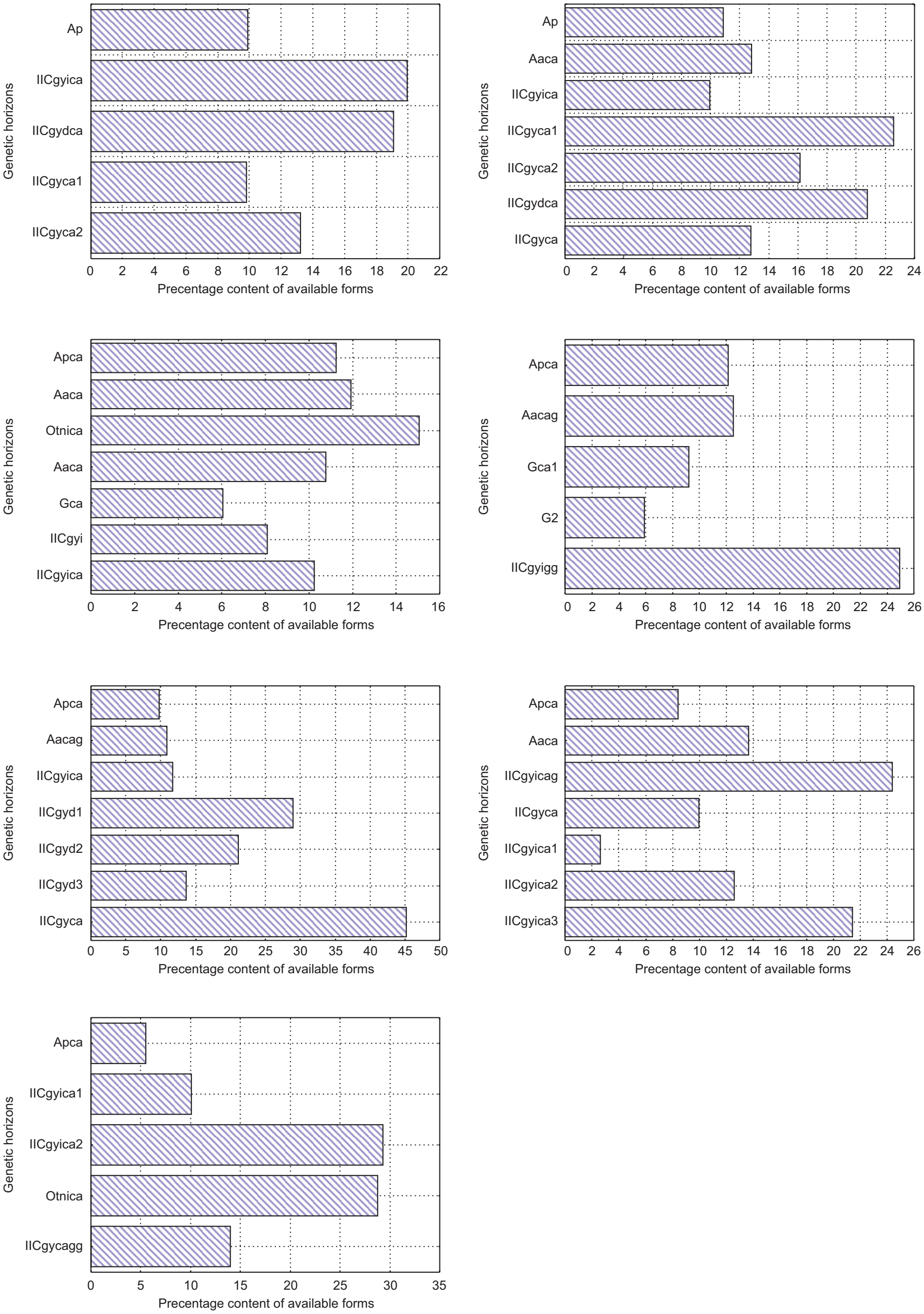

Fig. 2. Percentage content of available nickel forms in the soils

light soils, while the highest – in heavy soils. As reported by Dudek et al [37], in the unpolluted light soils about 65 % of nickel shows a strong bonding with the crystal structure of primary and secondary minerals. Warda [38] draws attention to the fact that an important factor modifying the uptake and the content of nickel by plants is not only the soil type, but mostly the plant species.

Conclusions

1. Drawing on the total content of the element investigated, the soils were considered to be the soils of a natural content of nickel and, as such, they can be allocated to horticultural and agricultural crops.
2. The low concentrations of total Ni suggest that those are natural contents (the geochemical background) and there is no clear effect of the anthropogenic activity on the soils.
3. The contents of the nickel forms extracted with DTPA fell within the range from $0.14\ \mathrm{mg \cdot kg^{-1}}$ to $2.86\ \mathrm{mg \cdot kg^{-1}}$ and those are the contents below the values considered toxic.

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ZAWARTOŚĆ FORM CAŁKOWITYCH I PRZYSWAJALNYCH NIKLU W ALUWIALNYCH GLEBACH UPRAWNYCH

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Abstrakt: Położone w dolinach rzecznych aluwia stanowią zróżnicowaną pokrywę glebową, na którą składają się zarówno gleby mineralne, mineralno-organiczne, jak i organiczne o bardzo zróżnicowanych właściwościach fizykochemicznych. Przedmiotem badań było określenie zawartości niklu w glebach aluwialnych wytworzonych na gytiach równiny biogennej Basenu Unisławskiego. Próbki glebowe pobrano z 7 profili glebowych, w których oznaczono wybrane właściwości fizykochemiczne metodami powszechnie stosowanymi w laboratoriach gleboznawczych. W analizowanych próbkach dokonano pomiaru całkowitej zawartości niklu po mineralizacji w mieszaninie kwasów HF + $HClO_4$ oraz jego form łatwo przyswajalnych, ekstrahowanych 1 M kwasem dietylenotriaminopentaoctowym (DTPA). Zawartość całkowitą oraz formy mobilne oznaczono przy zastosowaniu metody atomowej spektroskopii absorpcyjnej (AAS) na spektrometrze PU 9100X (Philips). Całkowita zawartość niklu mieściła się w zakresie (0,6; 18,04) mg $\cdot$ kg^{-1}. Największe zawartości tego pierwiastka odnotowano w poziomach powierzchniowych i podpowierzchniowych oraz w poziomach wzbogaconych w materię organiczną. W badanych próbkach glebowych stwierdzone całkowite zawartości niklu były zbliżone do zawartości tła geochemicznego. Natomiast zawartości form mobilnych była niższa od wartości uznanych za toksyczne. W badanych glebach zawartości form ekstrahowanych DTPA kształtowały się w zakresie (0,14; 2,09) mg $\cdot$ kg^{-1}.

Słowa kluczowe: nikiel w glebie, gleby aluwialne, formy całkowite i ekstrahowane DTPA

DOI: 10.2428/ecea.2012.19(04)036 ECOL CHEM ENG A. 2012;19(4-5):353-360

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POLLUTION OF FERTILIZERS WITH HEAVY METALS

ZANIECZYSZCZENIE NAWOZÓW MINERALNYCH METALAMI CIĘŻKIMI

Abstract: The aim of presented investigations was a comparison of heavy metal content in mineral fertilizers used in Poland and determining the sources of their origin in the fertilizers. The methods assumed as referential in fertilizer analysis were used to assess the contents of Cd, Cr, Cu, Hg, Ni, Pb and Zn in 44 samples of mineral fertilizers, including 29 fertilizers containing phosphorus (2 superphosphates and 27 multicomponent fertilizers), 14 nitrogen fertilizers and 1 potassium salt.

Considerable amounts of heavy metals were determined only in phosphorous and multicomponent fertilizers. A small content of lead was assessed in nitrogen fertilizers and in potassium salt, whereas usually only trace amounts of the other metals were detected. In the group of phosphorus and multicomponent fertilizers zinc, chromium and nickel occur in the biggest quantities, whereas mercury and lead in the smallest ones. The potential main source of cadmium, chromium and zinc in fertilizers containing phosphorus is phosphorite raw material while the source of nickel in multicomponent fertilizers is admixtures of ground dolomite. The permissible content of cadmium (50 mg · kg^{-1}), lead (140 mg · kg^{-1}), or mercury (2 mg · kg^{-1}) were exceeded in none of the analyzed fertilizers or mineral fertilizers not used for liming.

Keywords: mineral fertilizers, heavy metals, sources of pollution

Introduction

Mineral fertilizers used as a source of nutrients for plants may sometimes have a negative impact on the environment, mainly on soil and waters. Soil pollution with heavy metals is particularly dangerous [1]. Small contents of these metals in nitrogen and potassium fertilizers do not pose any hazard of soil or plant contamination, however phosphorus and multicomponent fertilizers, and some industrial wastes used for soil deacidification are usually significant factor in heavy metal balance in the environment [2, 3].

Some research projects implemented at the beginning of the last decade in the rural area of the EU [4] demonstrated that at great diversification the applied phosphorus

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fertilizers contained among others on average: 13 mg Cd, 60 mg Cr, 26 mg Cu, 13 mg Pb and 236 mg Zn per 1 kg of fertilizer. Multicomponent fertilizers were characterized by a considerably lower content of these elements, whereas in nitrogen fertilizers respectively: 0.9; 3.4; 2.0; 1.9 and 5.0 mg $\cdot$ kg^{-1} were assessed.

Another source of heavy metals is sulphuric acid used at manufacturing fertilizers containing phosphorus in a water soluble form. However, the basic sources of metals polluting fertilizers containing phosphorus are phosphorites used as a source of phosphorus. African sedimentary phosphorites from Senegal, Togo, Tunisia, some Moroccan deposits and those from North Carolina (USA) contain over 250 mg Cd $\cdot$ kg^{-1} P [2, 5]. During chemical processing of these minerals, cadmium, like uranium, passes mostly into soluble phase and then, in result of technological process, to the fertilizers. It favours mobility of this element and its entering the food chain [6]. The other metals usually form hardly soluble salts and mostly pass to phosphogypsum.

Presented paper aims to compare heavy metal contents in mineral fertilizers used in Poland and determine the sources of these metals origin in fertilizers.

Materials and methods

Heavy metals content was determined in 44 samples of mineral fertilizers, including 2 superphosphates, 27 samples of two- and multicomponent fertilizers, 14 samples of nitrogen fertilizers and one potassium salt. The fertilizers originated from the following enterprises: “Anwil” S.A. Wloclawek, AUREPIO” Ltd., “FOSFAN” S.A. Szczecin, “LUBON” S.A., “POLICE” S.A. Police and Zaklady Azotowe in Tarnow-Moscice.

According to the recommended methods of fertilizer analysis [7], samples of the analyzed fertilizers were dissolved in nitric acid (1:1) with a supplement of redistilled hot water, and the content of Cd, Pb, Ni, Cu, Cr and Zn in the solution were assessed using ICP-AES Ultrace 238 spectrometer made by Jobin Yvon (France). Mercury contents were determined in a fresh weighed portion of fertilizer by means of AMA 254 mercury analyzer. The analyses were conducted in 2 replications and if the *relative standard deviation* (RSD) was higher than 5 %, two additional assessments were conducted.

Results and discussion

Two of the analysed multicomponent fertilizers containing phosphorus (Table 1) were enriched in microelements.

NPKMg fertilizer (No. 16) contained admixtures of boron and zinc, whereas NPKMgS (No. 23) had supplements of boron, manganese and zinc. These supplements were not included in the statistical characteristics of this fertilizer group presented in Table 1.

The executive Regulation of the Minister of Agriculture and Rural Development referring to some provisions of the law on fertilizers and fertilization [8], stated among others permissible contents of arsenic, cadmium, lead and mercury in mineral fertilizers not used for liming. These are: 50 mg As and Cd, 140 mg Pb and 2 mg Hg $\cdot$ kg^{-1} d.m. of fertilizer. The quantities of cadmium, lead and mercury assessed in all analyzed fertilizers were much smaller than the above stated values. In the group of phosphorus

Table 1

Heavy metals content in investigated phosphorus and multicomponent fertilizers

Sample numbers	Chemical composition of fertilizer	Cd	Cr	Cu	Hg	Ni	Pb	Zn
		[mg · kg^{-1}]						
1	P = 19	10.74	102.8	9.5	0.132	23.0	2.11	115
2	P = 20	10.41	115.8	20.6	0.064	23.8	4.15	221
3	NPS = 18 – 46 – 5	19.09	274.7	17.6	0.025	36.4	0.82	306
4	PKMgS = 16 – 25 – 2 – 15	10.94	78.5	4.7	0.063	53.5	1.77	95
5	PKMgS = 10 – 20 – 4 – 15	6.06	75.3	6.8	0.105	107.1	1.47	51
6	PKS = 14 – 14 – 23	7.74	69.6	8.4	0.188	15.0	2.09	81
7	PKMgS = 10 – 20 – 2 – 15	7.55	67.6	16.7	0.263	78.8	1.9	93
8	PKS = 11 – 22 – 18	7.57	64.3	14.1	0.103	19.3	1.07	100
9	PKMgS = 12 – 20 – 6 – 10	6.17	119.4	13.9	0.252	246.0	2.54	84
10	PKS = 14 – 24 – 11.5	9.07	83.5	14.9	0.258	71.5	6.49	280
11	NPKS = 4 – 11 – 11 – 27	6.86	65.4	21.6	0.258	20.9	2.25	144
12	NPKMg = 4 – 12 – 20 – 2	12.29	66.4	18.8	0.028	77.5	1.78	107
13	NPKMgS = 5 – 10 – 25 – 2 – 13	4.81	69.5	19.3	0.052	68.5	2.61	83
14	NPKMgS = 4 – 12 – 12 – 2 – 26	5.43	63.2	9.8	0.101	65.7	2.85	107
15	NPKMgS = 5 – 10 – 15 – 3 – 22	5.38	79.3	11.3	0.095	135.5	3.49	128
16	NPKMg = 5 – 10 – 21 – 3	7.64	87.53	13.43	0.071	68.27	4.95	2235*
17	NPKMg = 4 – 17 – 24 – 6	9.05	72.5	12.0	0.064	62.4	1.63	48
18	NPKMg = 3 – 13 – 25 – 6	3.29	52.4	9.4	0.053	55.7	1.93	69
19	NPKMgS = 3 – 13 – 25 – 6 – 10	4.35	61.8	10.5	0.058	59.8	2.17	78
20	NPKMg = 3 – 12 – 18 – 4	6.24	121.7	7.2	0.031	187.1	2.44	109
21	NPKMg = 11 – 8 – 20 – 2	3.33	71.4	5.7	0.024	84.1	4.12	68
22	NPKMg = 5 – 15 – 30 – 2	4.8	112.3	4.5	0.029	193.8	0.50	82
23	NPKMgS = 10 – 8 – 15 – 5 – 35	2.94	65.67	540*	0.019	104.7	4.31	4240*
24	NPKS = 6 – 20 – 30 – 7	6.29	109.9	4.6	0.037	59.3	0.61	126
25	NPKS = 8 – 24 – 24 – 9	8.5	123.2	6.4	0.034	36.4	1.14	162
26	NPKMgS = 5 – 10 – 20 – 7 – 9	3.37	168.7	10.7	0.017	396.0	1.59	77
27	NPKMgS = 12 – 12 – 12 – 2 – 27	4.02	114.5	4.1	0.028	160.9	3.51	71
28	NPKS = 8 – 11 – 24 – 17	3.17	38.7	1.7	0.031	7.6	0.56	64
29	NPKMgS = 4 – 12 – 32 – 2 – 9	4.96	112.2	2.1	0.036	85.1	1.42	101
Minimum content		3.17	38.7	1.7	0.017	7.6	0.50	48
Maximum content		19.09	274.7	21.6	0.263	396.0	6.49	306
Mean content		7.09	94.6	10.6	0.090	90.0	2.19	113
Relative standard deviation [%]		49.4	48.8	54.5	90.3	94.8	60.1	56.0

* Fertilizers supplemented with Cu and Zn – values not taken into account in statistical calculations.

containing fertilizers (Table 1) assessed cadmium contents were lower or much lower than 38 %, mercury lower than 13 % and lead lower than 5 % than the permissible values. On average, analysed phosphorus containing fertilizers had the highest concentrations of zinc, then chromium and nickel and the lowest content of mercury, lead and cadmium.

In the tested fertilizer group the most diversified were the contents of nickel and mercury, for which relative standard deviation was higher than 90 % (Table 1). Relative standard deviations describing diversification of the contents of the other assessed metals in the fertilizers were apparently lower, ranging from 48.8 % to 60.1 %. The most probable source of cadmium, chromium and zinc in fertilizers containing phosphorus are phosphorites used for their manufacturing. This is evidenced not only by the highest and statistically strongly significant values of correlation coefficients describing the relationship between these metals contents and phosphorus content in a fertilizer (Table 2), but also the fact that the biggest amounts of these metals were assessed in monobasic and dibasic ammonium phosphate (NPS = 18 – 46 – 5, No. 3, Table 1).

Table 2

Correlation coefficients (r) between macroelements and heavy metals content in investigated phosphorus and multicomponent fertilizers

Element	No. of samples	Cd	Cr	Cu (n – 1)	Hg	Ni	Pb	Zn (n – 2)
N	19	0.564**	0.655**	0.186	–0.089	0.075	0.047	0.657**
P	29	0.765***	0.771***	0.076	–0.270	–0.223	–0.251	0.645***
K	26	–0.135	–0.024	–0.394*	–0.387	–0.112	–0.386*	–0.038
Mg	18	–0.573*	–0.151	–0.146	–0.090	0.240	–0.268	–0.563*

r significant at: * $\alpha \le 0.05$, ** $\alpha \le 0.01$, *** $\alpha \le 0.001$.

Generally, increased amount of nickel is determined in the fertilizers which also have magnesium among their components. Very high diversification of nickel content in the tested fertilizers: 7.6–396.0 mg · kg^{-1} d.m. was caused by ground dolomite supplement in the fertilizers. The dependence was even more pronounced in the studies on a similar fertilizer group conducted several years ago [9]. Dolomite supplements to fertilizers used at that time might have been also more polluted with cadmium and zinc than currently applied magnesium raw materials, which dilute cadmium and zinc in the investigated fertilizers (negative coefficients of correlation between Cd and Zn contents and Mg content in the fertilizer – Table 2), while formerly they used to be a significant source of these metals concentrations in fertilizers.

A significant, although statistically weaker, in comparison with phosphorus, relationship should be noticed between the contents of nitrogen, cadmium, chromium and zinc in the analyzed fertilizers containing phosphorus (Table 2). The more nitrogen the fertilizer contained, the more polluted it used to be with these metals. Mercury, like copper and lead contents in a fertilizer does not show any apparent dependence on any of the analyzed macroelements making up the studied fertilizers.

The rates of phosphorus and multicomponent fertilizers are usually determined on the basis of their phosphorus contents. Therefore, the results of conversion of the heavy metal amount assessed in the analyzed fertilizers with reference to phosphorus content in these fertilizers were compiled in Table 3.

Table 3

Heavy metals content in investigated phosphorus and multicomponent fertilizers

No. of sample	Chemical composition of fertilizer	Cd	Cr	Cu	Hg	Ni	Pb	Zn
		$[\mathrm{mg \cdot kg^{-1}\ P_2O_5}]$						
1	P = 19	56.5	541.2	50.2	0.695	121	11.1	605
2	P = 20	52.1	579.0	102.9	0.320	119	20.8	1105
3	NPS = 18 – 46 – 5	41.5	597.2	38.3	0.054	79	1.8	665
4	PKMgS = 16 – 25 – 2 – 15	68.4	490.8	29.6	0.394	334	11.1	594
5	PKMgS = 10 – 20 – 4 – 15	50.5	627.3	56.8	0.875	892	12.3	425
6	PKS = 14 – 14 – 23	55.3	497.1	59.9	1.343	107	14.9	579
7	PKMgS = 10 – 20 – 2 – 15	75.5	676.0	167.0	2.630	788	19.0	930
8	PKS = 11 – 22 – 18	68.8	584.5	128.2	0.936	175	9.7	909
9	PKMgS = 12 – 20 – 6 – 10	51.4	995.0	116.1	2.100	2050	21.2	700
10	PKS = 14 – 24 – 11.5	64.8	596.4	106.4	1.843	511	46.4	2000
11	NPKS = 4 – 11 – 11 – 27	62.4	594.5	196.4	2.345	190	20.5	1309
12	NPKMg = 4 – 12 – 20 – 2	102.4	553.6	156.7	0.233	646	14.8	892
13	NPKMgS = 5 – 10 – 25 – 2 – 13	48.1	695.0	193.0	0.520	685	26.1	830
14	NPKMgS = 4 – 12 – 12 – 2 – 26	45.3	526.8	81.3	0.842	547	23.8	892
15	NPKMgS = 5 – 10 – 15 – 3 – 22	53.8	793.3	113.0	0.950	1355	34.9	1280
16	NPKMg = 5 – 10 – 21 – 22	76.4	875.3	134.3	0.710	683	49.5	22350*
17	NPKMg = 4 – 17 – 24 – 6	53.2	426.5	70.6	0.376	367	9.6	282
18	NPKMg = 3 – 13 – 25 – 6	27.4	436.7	78.3	0.442	464	16.1	575
19	NPKMgS = 3 – 13 – 25 – 6 – 10	33.5	475.4	80.8	0.446	460	16.7	600
20	NPKMg = 3 – 12 – 18 – 4	52.0	1014	59.8	0.258	1559	20.3	908
21	NPKMg = 11 – 8 – 20 – 2	41.6	892.5	71.4	0.300	1051	51.5	850
22	NPKMg = 5 – 15 – 30 – 2	32.0	748.7	30.0	0.193	1292	3.3	547
23	NPKMgS = 10 – 8 – 15 – 5 – 35	36.8	820.9	6750*	0.238	1309	53.9	53000*
24	NPKS = 6 – 20 – 30 – 7	31.5	549.5	23.2	0.185	297	3.1	630
25	NPKS = 8 – 24 – 24 – 9	35.4	513.3	26.8	0.142	152	4.8	675
26	NPKMgS = 5 – 10 – 20 – 7 – 9	33.7	1687	107.4	0.170	3960	15.9	770
27	NPKMgS = 12 – 12 – 12 – 2 – 27	33.5	954.3	33.9	0.233	1341	29.3	592
28	NPKS = 8 – 11 – 24 – 17	28.8	352.1	15.4	0.282	69	5.1	582
29	NPKMgS = 4 – 12 – 32 – 2 – 9	41.3	935.0	17.5	0.300	709	11.8	842
Mean content		50.1	690.7	83.7	0.702	769	20.0	798

* Fertilizers supplemented with Cu and Zn – values not taken into account in statistical calculations.

The higher the content of "pure component" in a fertilizer, the smaller fertilizer mass is supplied to the soil. For this reason in 2002, Scientific Committee of Toxicology, Ecotoxicity and the Environment operating by the European Commission [2, 4] suggested a three-stage programme of decreasing the maximum cadmium content in fertilizers: by 2006 – 60 mg Cd, by 2010 – 40 mg Cd and by 2015 – 20 mg Cd $\cdot$ $\mathrm{kg^{-1}\ P_2O_5}$. Reduction of cadmium content in fertilizers to the level of below 20 mg Cd $\cdot$ $\mathrm{kg^{-1}}$

P_2O_5 at many-year application of these fertilizers should lead to maintaining this metal content in soil on an equal level or even its decrease.

The fertilizers presented in this paper, were manufactured in 2005. Average content of cadmium in the tested fertilizers containing phosphorus was 50.1 mg · kg^{-1} P_2O_5, which was by 21.6 mg · kg^{-1} P_2O_5 lower in comparison with this metal content in a similar group of fertilizers manufactured in Poland in 1993–1994 [9]. The level of cadmium pollution 60 mg · kg^{-1} P_2O_5 was exceeded in 7 analysed fertilizers (Table 3). A three-component mixed fertilizer with magnesium supplement was most burdened with this metal (102.4 mg Cd · kg^{-1} P_2O_5). Pollution of the studied fertilizers with mercury and lead, with reference to their phosphorus contents, was visibly lower in comparison with cadmium, whereas the contents of chromium, copper and zinc in these fertilizers should not raise objections.

The analyzed nitrogen fertilizers and concentrated potassium salt contained lower (and in some cases trace) amounts of the assessed metals (Table 4). Lead was the exception, as it occurred in these fertilizers in concentrations on average over twice higher in comparison with the fertilizers containing phosphorus (see Table 1). Only trace amounts of the analysed metals, particularly cadmium and lead, were detected in the analysed urea and ammonium nitrate. Nitro-chalks, mainly those containing magnesium, had slightly elevated contents of the studied metals.

Table 4

Heavy metals content in investigated nitrogen and potassium fertilizers

No. of sample	Chemical composition of fertilizer	Cd	Cr	Cu	Hg	Ni	Pb	Zn
		[mg · kg^{-1}]						
1	N = 46	0.03	1.71	0.65	0.031	0.63	0.59	42
2	N = 46	0.01	0.30	0.69	0.032	0.40	0.30	22
3	N = 34	0.01	0.35	1.49	0.023	0.78	0.38	26
4	NCa = 32 – 2	0.08	1.67	0.82	0.021	0.47	3.79	58
5	NCaMg = 30 – 4 – 2	0.13	1.09	0.57	0.024	0.56	7.58	64
6	NMg = 27 – 4	0.05	0.51	1.37	0.022	0.54	6.54	49
7	NCaS = 27 – 7.5 – 4.5	0.03	0.23	1.65	0.024	0.43	2.82	14
8	NCaMg = 27.5 – 6 – 4	0.11	0.57	0.95	0.021	0.48	6.45	41
9	NCaMgB = 27.5 – 6 – 4 – 0.2	0.10	0.69	0.67	0.022	0.52	6.53	55
10	NCaS = 27.5 – 6 – 4	0.08	0.44	1.07	0.019	0.41	2.81	34
11	NCaMg = 27.5 – 6 – 4	0.14	0.67	0.95	0.023	0.68	7.09	47
12	NCaMg = 27 – 6 – 3	0.28	1.73	0.72	0.006	0.87	15.05	114
13	NCaMgB = 27 – 6 – 3 – 0.2	0.20	1.07	0.62	0.005	0.67	10.91	71
14	N = 21	0.03	1.07	0.35	0.002	0.73	0.39	21
15	K = 60	0.01	0.29	1.17	0.011	0.55	1.31	20
Mean content		0.09	0.83	0.92	0.019	0.58	4.84	45

Also small content of the assessed metals in the concentrated (60 % K_2O) potassium salt should be emphasized (Table 4). This fertilizer is composed almost exclusively of potassium chloride releasing from the potassium bearing minerals, when the components not containing potassium are rejected [1]. Most probably, less concentrated potassium salts, with greater share of ballast would have been more polluted with heavy metals. Concentrated potassium salt added in production of mixed and complex multicomponent fertilizers (PK and NPK) may be the source of potassium, since it may slightly dilute the contents of heavy metals in these fertilizers. It seems to be confirmed also by negative values of all correlation coefficients describing the dependencies between the content of potassium and individual heavy metals in the tested two- and threecomponent fertilizers (Table 2).

Conclusions

1. Considering the analyzed fertilizers, significant contents of heavy metals were assessed only in phosphorus and multicomponent fertilizers. In nitrogen fertilizers and potassium salt only small content of lead was detected, whereas the other metals occurred in trace amounts.
2. In the group of phosphorus and multicomponent fertilizers, zinc occurs in the greatest amounts, then chromium and nickel, whereas mercury and lead in the smallest.
3. The main sources of cadmium, chromium and zinc in fertilizers containing phosphorus is phosphorite raw material, while nickel in multicomponent fertilizers comes from the used admixtures of ground dolomite.
4. Permissible contents of cadmium (50 mg $\cdot$ kg^{-1}), lead (140 mg $\cdot$ kg^{-1}) were exceed in none of the analyzed fertilizers and mercury (2 mg $\cdot$ kg^{-1}) in mineral fertilizers not used for liming.

Acknowledgements

The Authors wish to thank Ms Marzena Kendys, MSc. for her participation and involvement in conducting chemical analyses of the fertilizers discussed in this paper.

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ZANIECZYSZCZENIE NAWOZÓW MINERALNYCH METALAMI CIĘŻKIMI

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Abstrakt: Celem prezentowanych badań było porównanie zawartości metali ciężkich w nawozach mineralnych stosowanych w Polsce oraz określenie źródeł pochodzenia tych metali w nawozach. Metodami przyjętymi jako referencyjne w analizie nawozów, określono zawartość Cd, Cr, Cu, Hg, Ni, Pb i Zn w 44 próbkach nawozów, w tym 29 zawierających fosfor (2 superfosfatach i 27 nawozach wieloskładnikowych), w 14 nawozach azotowych i 1 soli potasowej.

Znaczące zawartości metali ciężkich stwierdzono tylko w nawozach fosforowych i wieloskładnikowych. W nawozach azotowych i w soli potasowej oznaczono jedynie niedużą zawartość ołowiu, a pozostałe metale najczęściej wykrywano w ilościach śladowych. W grupie nawozów fosforowych i wieloskładnikowych, w największych ilościach występuje cynk, chrom i nikiel, a w najmniejszych rtęć i ołów. Głównym źródłem kadmu, chromu i cynku w nawozach zawierających fosfor jest najprawdopodobniej surowiec fosforytowy, a niklu w nawozach wieloskładnikowych stosowane domieszki zmielonego dolomitu. W żadnym badanym nawozie nie zostały przekroczone dopuszczalne zawartości kadmu (50 $mg \cdot kg^{-1}$), ołowiu (140 $mg \cdot kg^{-1}$) i rtęci (2 $mg \cdot kg^{-1}$) w nawozach mineralnych nie służących do wapnowania.

Słowa kluczowe: nawozy mineralne, metale ciężkie, źródła zanieczyszczenia metalami ciężkimi

DOI: 10.2428/ecea.2012.19(04)037 ECOL CHEM ENG A. 2012;19(4-5):361-368

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EFFECT OF SOME SUBSTANCES ON THE CONTENT OF ORGANIC CARBON AND MINERAL COMPONENTS IN SOILS CONTAMINATED WITH CHROMIUM

WPŁYW NIEKTÓRYCH SUBSTANCJI NA ZAWARTOŚĆ WĘGLA ORGANICZNEGO I SKŁADNIKÓW MINERALNYCH W GLEBACH ZANIECZYSZCZONYCH CHROMEM

Abstract: The aim of the study was to determine the effects of compost, zeolite and CaO used as neutralizing substances on the content of organic carbon and mineral components in soils contaminated with Cr(III) and Cr(VI).

The content of organic carbon and mineral components varied depending on the form and the dose of chromium and neutralizing substances used. Increasing contamination of soil with Cr(III) and Cr(VI) resulted in the growth of the content of organic carbon and available forms of potassium and chromium(VI) resulted in a reduction of the content of available magnesium. Among the substances applied, compost and zeolite had larger effects than calcium oxide on the examined properties of soil, particularly in the case of organic carbon, phosphorus and magnesium. Compost and zeolite resulted in increasing the content of organic carbon and magnesium, and decreasing the content of phosphorus in the soil.

Keywords: chromium contamination, compost, zeolite, CaO, soil, organic carbon, available mineral components

Progressive degradation of the natural environment, a consequence of technological development, results in increasing contamination of the environment with xenobiotics. These include heavy metals detrimental to the natural environment, such as chromium. Chromium compounds most often found in the natural environment are of the +3 and +6 oxidation state. They differ in chemical properties as well as in their chemical and biological reactivity [1]. Chromium(III) found in a polluted natural environment is insoluble and mobile only to a slight extent, but the presence of organic ligands (*eg* humic, fulvic acids) causes complexation of Cr(III). This results in increasing solubility

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of trivalent chromium, hence its improved mobility and accessibility for living organisms. Chromium(VI) is regarded as more accessible due to its solubility, strong oxidizing properties and permeability through cell membranes [2].

The aim of the research conducted was to determine the effect of soil contamination with increasing doses of trivalent and hexavalent chromium on the content of organic carbon, available forms of phosphorus, magnesium and potassium in the soil, and to determine the role of the additives – compost, zeolite and calcium oxide – in mitigating the results of this contamination.

Material and methods

The experiment with 4 replicates was established in the vegetation hall of the University of Warmia and Mazury in Olsztyn (Poland) in polyethylene pots of 9.5 kg capacity in 2007. The soil of granulometric composition of loamy sand was characterized by the following properties: pH_{KCl} – 4.4, *hydrolytic acidity* (HA) – 44.00 $mmol(H^+) \cdot kg^{-1}$ soil, sum of *exchangeable base cations* (EBC) – 90.00 $mmol \cdot kg^{-1}$, *cation exchangeable capacity* (CEC) – 134.00 $mmol \cdot kg^{-1}$, *base saturation* (BS) – 67.16 %, content of C_{org} – 5.63 $g \cdot kg^{-1}$, content of available: phosphorus – 55.15 $mg \cdot kg^{-1}$, potassium – 56.27 $mg \cdot kg^{-1}$ and magnesium – 50.39 $mg \cdot kg^{-1}$. Normal brown soil under natural conditions was used. Before placing in pots, the soil was contaminated with water solutions of chromium(III) in the form of $KCr(SO_4)_2 \cdot 2H_2O$ and chromium(VI) in the form of $K_2Cr_2O_7$ in the following amounts: 0 (control), 25, 50, 100 and 150 $mg\ Cr \cdot kg^{-1}$ of the soil. Basic macro- and microelements were introduced to the soil in the following amounts (per 1 kg of the soil): 110 mg N [$CO(NH_2)_2$ + $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ + $(NH_4)_2HPO_4$], 50 mg P [$(NH_4)_2HPO_4$], 110 mg K [KCl + $KCr(SO_4)_2 \cdot 12H_2O$ + $K_2Cr_2O_7$], 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 [$H_3BO_3$], as well as additives mitigating the effects of chromium: compost and zeolite in the amount of 3 % in relation to the weight of the soil, and calcium oxide in the amount equal to 1 hydrolytic acidity (Hh). The experiment involved cultivation of spring rape (*Brassica napus* var. *oleifera*) – main crop and yellow lupin (*Lupinus luteus* L.) – successive crop. The density of spring rape was 25 pieces per pot, and yellow lupin was 18 pieces. Spring rape and yellow lupin were harvested in the blossoming phase.

Before establishing the experiment and after the harvest of crops, samples of soil were taken from each pot, dried at room temperature, crushed and sieved through a 1 mm mesh. In the material obtained, selected properties were analysed using the following methods: content of *organic carbon* (C_{org}) – according to the Tiurin method in potassium dichromate with dilute sulfuric(VI) acid [3], content of phosphorus and magnesium – according to the Egner-Riehm method [3], content of magnesium – according to Schachtschabel method [3]. The obtained results were statistically analysed with the use of STATISTICA software [4] using an ANOVA three-factor analysis of variance (1^{st} factor – contamination type, 2^{nd} factor – chromium dose, 3^{rd} factor – type of neutralizing substance). The correlation between chromium dose and content of organic C and macroelements in soil was also calculated.

Results and discussion

Soil contamination with chromium(III) and chromium(VI) as well as the neutralizing additives applied significantly modified the content of organic carbon in the examined soil (Table 1).

In the series without neutralizing additives, increasing soil contamination with Cr(III) and Cr(VI) resulted in a significant growth of the content of organic carbon in the examined soil. Soil contaminated with trivalent chromium revealed a slightly higher content of organic carbon. Neutralizing additives in the form of compost, zeolite and calcium oxide significantly affected the content of the component under discussion. The application of zeolite in the series with chromium(VI) proved most beneficial, resulting in the growth of the mean content of organic carbon by 21 % in relation to the control series. The application of calcium oxide contributed to a significant reduction in the mean content of organic carbon in both contamination variants. However, the effect of CaO was larger in objects with chromium(III).

The content of available phosphorus was at a varied level, depending on the dose and the form of chromium, as well as on the application of compost, zeolite and calcium oxide (Table 2). Doses of 25 and 50 cm^3 of Cr(VI) $\cdot$ kg^{-1} of soil most strongly reduced the content of phosphorus with reference to the control object. In the series with Cr(III), a dose of 100 $cm^3 \cdot kg^{-1}$ of soil most strongly affected the content of the component under discussion, causing its 28 % reduction in relation to the control series. Compost and zeolite had a negative effect on the concentration of available phosphorus in soil contaminated both with trivalent and hexavalent chromium. Additionally, an increase of phosphorus content was also observed after applying CaO in objects with Cr(III).

The content of available potassium in the examined soil was affected by the dose and the form of chromium, as well as mitigating additives used in the experiment (Table 2).

A higher average content of potassium was revealed by objects contaminated with chromium(VI). Increasing doses of trivalent and hexavalent chromium in the control series had a positive effect on the content of available potassium in the soil. In objects with Cr(VI), this effect was higher, since it resulted in an almost three-fold increase in the content of the component under discussion. Among the substances applied, the strongest effects were caused by compost, which reduced the average content of available potassium in the soil, particularly in objects with chromium(VI). An increase in the potassium content in soil was also found after application of zeolite, but only in pots with chromium(III).

The effect of soil contamination with Cr(III) and Cr(VI) on the content of available magnesium was modified by the amount of the dose and by addition of neutralizing substances to the soil (Table 2). Hexavalent chromium in the control series resulted in a significant reduction in available magnesium concentration in the analysed soil, however, it was not a clearly oriented effect. An exception was contamination with 25 cm^3 Cr(VI) $\cdot$ kg^{-1} of soil, which increased the content of the component under discussion by a few percent. Among the mitigating substances, the addition of compost had the strongest effect on the average content of magnesium, and the lowest effect was the addition of zeolite.

Table 1

C_{org} content in soil after crop harvest [g · kg^{-1} d.m. of soil]

Cr dose [mg · kg^{-1} of soil]	Chromium(III)					Chromium(VI)				
	Type of neutralizing substance									
	Without additions	Compost	Zeolite	CaO	Average	Without additions	Compost	Zeolite	CaO	Average
0	6.00	6.08	9.75	5.85	6.92	6.00	6.08	9.75	5.85	6.92
25	6.98	6.23	8.85	5.48	6.89	6.83	7.28	7.50	7.13	7.19
50	7.50	8.10	7.80	5.10	7.13	7.20	7.88	7.73	6.23	7.26
100	7.65	8.33	6.23	6.15	7.09	7.58	8.18	8.33	6.00	7.52
150	7.88	8.85	6.00	5.85	7.15	7.80	9.68	9.60	5.78	8.22
Average	7.20	7.52	7.73	5.69	7.04	7.08	7.82	8.58	6.20	7.42
r	0.864**	0.905**	–0.961**	0.377	0.801**	0.921**	0.962**	0.229	–0.438	0.972**
LSD	a – 0.10**, b – 0.16**, c – 0.14**, a · b – 0.22**, a · c – 0.20**, b · c – 0.32**, a · b · c – 0.45**									

LSD for: a – contamination type, b – chromium dose, c – type of neutralizing substance; n.i. – insignificant differences; * and ** – difference significant at p = 0.05 and p = 0.015, respectively; r – correlation coefficient calculated between chromium dose and C_{org} content in soil.

Table 2

Content of available phosphorus, potassium and magnesium in soil after crop harvest [mg · kg^{-1} d.m. of soil]

Cr dose [mg · kg^{-1} of soil]	Chromium(III)					Chromium(VI)				
	Type of neutralizing substance									
	Without additions	Compost	Zeolite	CaO	Average	Without additions	Compost	Zeolite	CaO	Average
	Phosphorus									
0	137.8	84.4	62.6	179.7	116.1	137.8	84.4	62.6	179.7	116.1
25	101.6	79.4	65.4	159.6	101.5	83.6	83.0	68.3	110.0	86.2
50	100.9	68.6	75.6	176.4	105.4	97.3	84.6	75.7	94.6	88.1
100	99.7	63.7	80.9	152.9	99.3	122.3	90.1	97.1	89.5	99.8
150	102.7	59.5	84.0	129.0	93.8	129.8	95.8	112.9	85.8	106.1
Average	108.5	71.1	73.7	159.5	103.2	114.2	87.6	83.3	111.9	99.3
r	–0.588	–0.951**	0.952**	–0.893**	–0.726*	0.283	0.951**	0.996**	–0.753**	–0.314
LSD	a – 1.85**, b – 2.93**, c – 2.62**, a · b – 4.15**, a · c – 3.71**, b · c – 5.88**, a · b · c – 8.30**									
	Potassium									
0	15.7	15.7	17.3	20.6	17.3	15.7	15.7	17.3	20.6	17.3
25	15.7	15.7	19.0	19.0	17.3	20.6	15.7	22.2	30.3	22.2
50	17.3	15.7	22.2	15.7	17.7	36.8	19.0	28.7	33.6	29.5
100	19.0	17.3	28.7	15.7	20.2	41.7	22.2	36.8	35.2	34.0
150	20.6	15.7	30.3	15.7	20.6	43.3	23.8	43.3	43.3	38.4
Average	17.7	16.0	23.5	17.3	18.6	31.6	19.3	29.7	32.6	28.3
r	0.987**	0.325	0.979**	–0.807**	0.893**	0.901**	0.974**	0.993**	0.936**	0.989**
LSD	a – 0.67**, b – 1.07**, c – 0.95**, a · b – 1.51**, a · c – 1.35**, b · c – 2.14**, a · b · c – 3.02**									

Table 2 contd.

Cr dose [mg · kg^{-1} of soil]	Chromium(III)					Chromium(VI)				
	Type of neutralizing substance									
	Without additions	Compost	Zeolite	CaO	Average	Without additions	Compost	Zeolite	CaO	Average
Magnesium										
0	53.6	55.6	48.6	41.4	49.8	53.6	55.6	48.6	41.4	49.8
25	50.4	61.6	48.2	51.3	52.9	58.6	60.1	66.4	42.9	57.0
50	52.1	63.1	53.3	50.7	54.8	51.3	69.2	63.4	43.5	57.9
100	53.8	66.4	60.3	49.9	57.6	49.6	76.4	56.2	45.2	56.9
150	54.8	69.6	63.8	50.5	59.7	43.0	76.8	61.2	45.6	56.6
Average	52.9	63.3	54.8	48.8	55.0	51.2	67.6	59.2	43.7	55.6
r	0.619*	0.956**	0.978**	0.538	0.979**	–0.879**	0.932**	0.241	0.964**	0.665*
LSD	a – 0.38*, b – 0.60**, c – 0.54**, a · b – 0.85**, a · c – 0.76**, b · c – 1.21**, a · b · c – 1.71**									

r – correlation coefficient calculated between chromium dose and content of macroelements (P or K or Mg) in soil. Other explanations under Table 1.

The accumulation of heavy metals in the soil can result in various changes to its properties [5]. On one hand, the soil fulfils the role of a filter which protects against contamination, while on the other, it acts as an intermediary in transporting contaminants [6]. In the authors' own research, soil contamination with compounds of chromium(III) and (VI) significantly modified the content of organic soil and mineral components in soils. Nutrient content affects the growth of cultivated crops to a large extent [7]. Chromium, especially high doses of chromium(VI), have a large negative effect on number of microorganisms [8–10] and enzymatic activity in soil [8–11]. Microorganisms take participation in biochemical transformations of nutrients in soil and in consequences they decided about content of available macroelements (eg phosphorus, calcium and magnesium) in soil. By applying various types of neutralizing substances to the soil, it is possible to positively affect soil conditions. The positive effect of zeolites results from their high porosity and sorptive capacity which, as in the authors' own research, was also confirmed by Ouki et al [12], Silva et al [13] and Leyva-Ramos et al [14]. Soil liming has a positive effect on their reaction, creates favourable conditions for the growth of microorganisms and consequently, accelerates processes of organic matter mineralization [15]. The application of calcium oxide in the experiment with Cr(III) had a favourable effect on the content of available phosphorus, but it significantly reduced the content of organic carbon in both contamination variants. The use of composts positively influences the physicochemical properties of soils, including soil contamination with chromium [16], which is also proved by own research.

Conclusions

1. The content of organic carbon and mineral component was varied depending on the form and the dose of chromium, as well as on the neutralizing substances used.
2. Increasing contamination of soil with Cr(III) and Cr(VI) resulted in the growth of the content of organic carbon and available forms of potassium, and Cr(VI) in a reduction of the content of available magnesium.
3. Among the substances applied, compost and zeolite had effects on the examined properties of soil larger than calcium oxide, particularly in the case of organic carbon, phosphorus and magnesium. Compost and zeolite resulted in increasing the content of organic carbon and magnesium and decreasing the content of phosphorus in soil.

Acknowledgements

The study has been performed as part of research funded by the Polish Ministry of Science and Higher Education No. N N305 1059 33.

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WPŁYW NIEKTÓRYCH SUBSTANCJI NA ZAWARTOŚĆ WĘGLA ORGANICZNEGO I SKŁADNIKÓW MINERALNYCH W GLEBACH ZANIECZYSZCZONYCH CHROMEM

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Abstrakt: Celem badań było określenie oddziaływania kompostu, zeolitu i CaO, stosowanych jako substancje neutralizujące, na zawartość węgla organicznego i składników mineralnych w glebach zanieczyszczonych Cr(III) i Cr(VI).

Zawartość węgla organicznego i składników mineralnych wykazywała znaczne zróżnicowanie w zależności od formy i dawki chromu oraz użytych substancji neutralizujących. Wzrastające zanieczyszczenie gleby Cr(III) i Cr(VI) spowodowało wzrost zawartości węgla organicznego oraz przyswajalnych form potasu, a chrom(VI) obniżenie zawartości przyswajalnego magnezu. Spośród zastosowanych substancji kompost i zeolit miały większy niż tlenek wapnia wpływ na badane właściwości gleby, zwłaszcza w przypadku węgla organicznego, fosforu i magnezu. Kompost i zeolit spowodowały wzrost zawartości węgla organicznego i magnezu oraz zmniejszenie zawartości fosforu w glebie.

Słowa kluczowe: zanieczyszczenie chromem, kompost, zeolit, CaO, gleba, węgiel organiczny, przyswajalne składniki mineralne

DOI: 10.2428/ecea.2012.19(04)038 ECOL CHEM ENG A. 2012;19(4-5):369-376

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INFLUENCE OF NITROGEN DOSES APPLIED IN SEWAGE SLUDGE ON THE CONTENT OF MACROELEMENTS IN THE WILLOW (*Salix viminalis*)

WPŁYW DAWEK AZOTU ZASTOSOWANEGO W OSADZIE ODCIEKOWYM NA ZAWARTOŚĆ MAKROELEMENTÓW W WIERZBIE (*Salix viminalis*)

Abstract: The influence of different doses of nitrogen applied in the sewage sludge as well as NPK in mineral fertilizers in the field experiment carried out during three years on the content of macroelements in the willow biomass *Salix viminalis* was the aim of this work. The doses of nitrogen applied in the form of sewage sludge reached 100, 150 and 200 kg · ha^{-1}. Besides those objects field experiment contained two more objects: NPK with N-150, P-50, and K 150 kg · ha^{-1} in which every year 50 kg of N in urea form was applied with P and K at ratio maintained above and in control. The content of determinated elements P, K, S, Ca, Mg and Na in the branches of willow was not significantly differentiated upon the influence of different nitrogen doses applied in the form of sewage sludge. The content of potassium and sulfur was significantly higher in branches of willow harvested from the object fertilized with doses of nitrogen 200 kg N · kg^{-1} then from others objects. The content of potassium, sulfur, calcium, magnesium and sodium in the branches of willow biomass was not significantly differentiated upon the investigated parameters, but the content of phosphorus was significantly lower in biomass harvested from objects fertilized with sewage sludge than mineral fertilizers. The highest amount of determinated elements was taken up by willow cultivated in the second year and the lowest in the first year of experiment. The uptake of phosphorus increased in each year of experiment from the lowest in the first year up to highest in the third year of experiment.

Keywords: sewage sludge, nitrogen, biomass of willow, macroelements

Introduction

The share of renewable energy in energetic balance of Poland in the 2020 year should reached up to 20 %. Solid biomass comes mainly as the waste from forestry, wood industry, meat and plant processing industry, municipal waste treatment and agriculture. It is predicate that in the future main source of biomass will be the

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plantation of energetic plants. The willow (*Salix viminalis*) is recognized especially in north European (Scandinavian) and North American lands as the very good plant with quick growth for harvesting of biomass for the energetic purpose [1–4]. Yield of the willow (*Salix viminalis*) cultivated and harvested in Poland and in another countries generally reach up to 15 MG (ton) $\cdot$ ha^{-1} dry matter [5–8].

The amount of plant nutrients introduce into the soil should be taken under consideration the fertility of soil as well as the uptake and the yield of those macro- and microelements. For the fertilization of willow can be used organic and mineral fertilizers as well as different waste for example sewage sludge, because this plant shows big possibility for the utilization of plant nutrients from those materials [9, 10] what allow good growth and high yield of this plant.

The aim of this investigation carried out as field experiment during the years 2002–2005 was the estimation of the influence of different nitrogen doses applied into the soil in the form of sewage sludge as well as mineral fertilizers on the content of phosphorus, potassium, calcium, magnesium, sulfur and sodium in the biomass (branches) of willow (*Salix viminalis*). The yield of biomass harvested in this experiment has been published in the other paper [9].

Materials and methods

The field experiment was laid down of spring 2002 year on the soil developed from loamy light sand (according to Polish Soil Science Society) and was carried out during three years. The soil had neutral reaction (pH measured in 1 mol $\cdot$ $CaCl_2$ dm^{-3} reached 6.5 unit) and the high content g $\cdot$ kg^{-1} (of d.m. soil) of organic carbon 42.5 and total nitrogen 2.50, respectively. The total content in g $\cdot$ kg^{-1} of estimated macroelements was as follows, respectively: P – 0.99, K – 1.71, Ca – 9.87, Mg – 1.69 and Na 0.21. The scheme of experiment contained follows objects: different doses of nitrogen applied with sewage sludge (kg $\cdot$ ha^{-1}): 100, 150 and 200; object fertilized with urea applied in 50 kg $\cdot$ ha^{-1} nitrogen in each year (total amount 150 kg $\cdot$ ha^{-1}) and control in which only phosphorus and potassium were applied.

Fresh sewage sludge produced on the municipal sewage purification plants at Siedlce was applied at spring before plantation of willow plant. The used sewage sludge contained 20.2 % of dry matter in which the following amount of investigated elements were determinated in g $\cdot$ kg^{-1} of d.m.: N – 50.6, P – 25.8, K – 3.25, Ca – 41.8, Mg – 8.90, S – 6.51, Na – 1.68 and in mg $\cdot$ kg^{-1} of d.m.: Fe – 13499, Mn – 253, Zn – 1573, Cu – 139, Mo – 5.92, Co – 5.10. The content of heavy metals in the sewage sludge was in the amount accepted for fertilizer use in agriculture [11].

The urea was applied in each year three times during whole duration of experiment in dose 50 kg N $\cdot$ ha^{-1} before the starting of vegetation. In the first year of experiment on all objects fertilized with sewage sludge, urea and control (without nitrogen) additional fertilization with potassium (potassium salt) in dose to reach the ratio N : K equal 1 : 1 was applied. On the object fertilized with urea additional fertilization with phosphorus and potassium were applied in the form of mineral fertilizer (triple superphosfate and potassium salt) in dose to reach the ratio of N : P : K equal 1 : 0.35 : 1. The amount of P and K applied in the control object equal to the amount of those elements introduced into the soil with the middle dose of sewage sludge which contained 150 kg · ha^{-1} of nitrogen.

The experiment was laid down in four replicates in which willow (*Salix viminalis*) clone 1056 was cultivated in the area plot on 8 m^2 and at the density 8 pieces of plant per 1 m^2. The biomass of willow was harvested in each year of experiment. Whole biomass of the willow branches were harvested in February. These branches were shreaded, representative samples were separated, dried and finely grounded. So prepared samples were digested by the "method of dry combustion" in the oven at the temperature 450 ^{o}C. Ash was treated by 6 mol HCl · dm^{-3} to decompose carbonate. The excess of HCl from crucible was evaporated to dryness. The chlorides of elements were transferred by 10 % HCl to volumetric flask. This was the base solution in which investigated elements were determined by ICP-AES method on the spectrometer Optima 3200 manufactured by Perkin-Elmer.

The results were statistically calculated using the analyses of variance for the experiment with two investigated parameters in completely randomized scheme. The values of LSD$_{0.05}$ were calculated by Tukey's test.

Results and discussion

The cultivation of willow in the every year harvesting system allow the production of biomass in small and big areas of energetic plants for it using in own farms or for sale to energetic plants in small towns. The cultivation of willow in this system makes easy its fertilization and harvesting [12]. Independently from the cycle of biomass harvesting system(every year or once per 3 years) to obtained high yield of biomass, it is necessary to applied high doses of plant nutrients, which can be supplied in organic and mineral fertilizers by mixing their with soil. Utilization of sewage sludge in fertilization this plant is quite possibility but needs to their cover (mixing) with soil. The sewage sludge used in this experiment for fertilization of willow, were the main source of macro- and microelements, beside some quantity of those elements which can be taken up by plants from soil. Sewage sludge applied in this experiment contained very low amount of potassium and therefore additional potassium dose was applied in mineral fertilizer.

The content of calcium and sodium in willow branches was not significantly differentiated by the doses of sewage sludge (Table 1). The content of Mg, K, P and S was significantly higher in the branches of willow harvested from the plots fertilized with the highest doses of sewage sludge (200 kg · ha^{-1} of nitrogen) and the lowest at medium doses of nitrogen (150 kg N · ha^{-1}). The willow biomass harvested from plants fertilized with sewage sludge in dose contained 150 kg · ha^{-1} of nitrogen contained lower content of phosphorus, potassium and sulfur than it biomass harvested from control object (fertilized only with PK). Content of calcium, magnesium and sodium in willow branches harvested from above described objects were similar. The content of all determinated elements in willow biomass harvested from the objects fertilized with urea were not significantly differentiated from the content of these element in biomass

Table 1

The content of determinated macroelements [g · kg^{-1} d.m.] in willow branches

Doses of nitrogen	Calcium				Magnesium				Potassium			
	Years of cultivation			Mean	Years of cultivation			Mean	Years of cultivation			Mean
	I	II	III		I	II	III		I	II	III	
Control object	4.86	7.11	4.81	5.59	0.656	0.734	0.585	0.658	14.19	3.30	3.62	7.04
100kg N (sludge)	4.28	6.00	4.81	5.03	0.563	0.719	0.670	0.651	10.59	4.01	4.05	6.22
150kg N (sludge)	4.20	3.82	6.04	4.69	0.525	0.543	0.700	0.589	9.75	1.88	3.78	5.14
200kg N (sludge)	4.10	7.51	4.53	5.38	0.649	0.710	0.589	0.649	12.04	4.03	3.99	6.69
150kg N (urea)	5.20	6.03	5.59	5.61	0.718	0.918	0.710	0.782	12.08	4.23	3.93	6.75
Mean	4.53	6.10	5.16	5.26	0.622	0.725	0.651	0.666	11.73	3.49	3.87	6.37
LSD$_{0.05}$	0.75*			n.i.***	0.090*			0.137**	0.95*			1.45**
	Sodium				Phosphorus				Sulfur			
Control object	0.137	0.589	0.011	0.246	2.25	1.05	1.31	1.54	0.866	0.600	0.346	0.604
100kg N (sludge)	0.106	0.664	0.024	0.265	1.62	1.23	1.33	1.39	0.623	0.594	0.361	0.526
150kg N (sludge)	0.131	0.633	0.020	0.261	1.66	0.58	1.44	1.23	0.573	0.447	0.375	0.465
200kg N (sludge)	0.129	0.625	0.014	0.256	1.89	1.18	1.41	1.49	0.777	0.586	0.364	0.576
150kg N (urea)	0.128	0.660	0.038	0.275	2.26	1.34	1.37	1.66	0.933	0.679	0.380	0.664
Mean	0.126	0.634	0.065	0.261	1.94	1.08	1.37	1.46	0.754	0.581	0.365	0.567
LSD$_{0.05}$	0.053*			n.i.***	0.15*			0.23**	0.070*			0.102**

* LSD$_{0.05}$ for years of cultivation, ** LSD$_{0.05}$ for fertilizations objects, *** n.i. – differences among average unimportant.

harvested from control object (only PK). Also the content of all investigated elements in biomass harvested from the objects fertilized with urea (object with mineral fertilizer) was slightly higher (most often not significantly differentiated) than in biomass harvested from objects fertilized with all doses of sewage sludge. Only the content of P, K, Mg and S was higher in willow biomass harvested from plants fertilized with urea (mineral fertilizers) than after sewage sludge applied with dose contained 150 kg · ha^{-1} of nitrogen.

The content of all determinated elements in willow biomass was significantly differentiated under the influence of the harvesting year. The highest concentration of phosphorus, potassium and sulfur were determinated in the willow biomass harvested in the first year of cultivation whereas the content of calcium, magnesium and sodium were the highest in the biomass harvested in the second year of cultivation. The lowest content of calcium and magnesium in the willow branches were determinated in first year of cultivation, but phosphorus and potassium in second year, however sodium and sulfur in third year.

The uptake of determinated elements (kg · ha^{-1}) by harvested part of willow (branches) was depended up their content in biomass (Table 1) and yield [9]. The amount of macroelements taken up by harvested biomass significantly depended upon investigated parameters; it is year of cultivation and different kind and dose of fertilizers (Table 2). The highest amount of P, K were taken up by willow biomass harvested in the third and the lowest in the first year of cultivation, whereas Ca, Mg, S and Na the highest in the second and the lowest in the first year of cultivation. It is also very interesting that the amounts of P and K taken up by willow biomass increased in each year of cultivation from the lowest in the first up to the highest in the third year of cultivation. The highest amount of investigated elements were harvested most often with biomass from plots fertilized with the highest dose of sewage sludge in which 200 kg · ha^{-1} of and the lowest with the dose 150 kg · ha^{-1} nitrogen introduces into the soil. The contents of P, K, Mg and S in biomass harvested from plants fertilized with urea (mineral fertilization) were not significantly differentiated from the amount of determinated elements harvested from control plots. The amount of determinated elements harvested with willow biomass from plots fertilized with sewage sludge in dose 100 kg · ha^{-1} and 200 kg · ha^{-1} of nitrogen generally was higher than from control plot.

The relation of chemical elements one- to bivalent ([K + Na]/[Ca + Mg] counted as their the gram-equivalents) in first year of the willow cultivation ranged from 0.99 in object fertilized with urea to 1.24 on control once (Table 3). The willow sprouts fertilized with sewage sludge had in first year the lowest relation of chemical elements one- to bivalent on object with dose 150 kg N · ha^{-1} (1.01), and the highest after applied dose 200 kg N · h^{-1} (1.22). Willow sprouts harvested in second and third year had the similar relation of chemical elements one- to bivalent (average value for all studied objects had value 0.32 and 0.33, respectively). It means that in the first year of cultivation willow plant have taken mainly potassium and sodium and much less calcium and magnesium. It is explained by physiology of this plant connected with the amount of woody materials which in the first year of cultivation is very low in whole biomass of willow branches.

Table 2

Uptake of determinated macroelements [kg · ha^{-1}] by willow

Doses of nitrogen	Calcium					Magnesium					Potassium				
	Years of cultivation			Mean	Sum	Years of cultivation			Mean	Sum	Years of cultivation			Mean	Sum
	I	II	III			I	II	III			I	II	III		
Control object	24.4	219.6	120.8	121.6	364.8	3.3	22.7	14.7	13.6	40.7	71.4	101.9	90.9	88.1	264.2
100 kg N (sludge)	26.2	203.2	133.6	121.0	363.0	3.4	24.4	18.6	15.5	46.4	64.7	135.8	112.5	104.3	313.0
150 kg N (sludge)	17.6	121.6	184.9	108.0	324.1	2.2	17.3	21.4	13.6	40.9	41.0	59.8	115.7	72.2	216.5
200 kg N (sludge)	26.7	262.3	166.8	151.9	455.8	4.2	24.8	21.7	16.9	50.7	78.4	140.8	146.9	122.0	366.1
150 kg N (urea)	16.7	163.5	143.4	107.9	323.6	2.3	24.9	18.2	15.1	45.4	38.8	114.7	100.8	84.8	254.3
Mean	22.3	194.0	149.9	122.1	366.2	3.1	22.8	18.9	14.9	44.8	58.9	110.6	113.4	94.3	282.9
LSD$_{0.05}$	8.5*			12.9**	—	1.9*			2.9**	—	6.8*			10.4**	—
	Sodium					Phosphorus					Sulfur				
Control object	0.7	18.2	0.3	6.4	19.2	11.3	32.4	32.9	25.5	76.6	4.4	18.5	8.7	10.5	31.6
100 kg N (sludge)	0.6	22.5	0.7	7.9	23.8	9.9	41.7	36.9	29.5	88.5	3.8	20.1	10.0	11.3	33.9
150 kg N (sludge)	0.6	20.1	0.6	7.1	21.3	7.0	18.5	44.1	23.2	69.6	2.4	14.2	11.5	9.4	28.1
200 kg N (sludge)	0.8	21.8	0.5	7.7	23.1	12.3	41.2	51.9	35.1	105.4	5.1	20.5	13.4	13.0	39.0
150 kg N (urea)	0.4	17.9	1.0	6.4	19.3	9.6	34.0	40.2	27.9	83.8	3.0	18.4	9.8	10.4	31.2
Mean	0.6	20.1	0.6	7.1	21.3	10.0	33.6	41.2	28.3	84.8	3.7	18.3	10.7	10.9	32.8
LSD$_{0.05}$	1.0*			1.5**	—	3.0*			4.5**	—	1.4*			2.1**	—

* LSD$_{0.05}$ for years of cultivation, ** LSD$_{0.05}$ for fertilizations objects.

Table 3

The ratio of chemical elements one- to bivalent (K + Na)/(Ca + Mg) calculated as gramequivalent

Doses of nitrogen	(K + Na) / (Ca + Mg)			
	Years of cultivation			Mean
	I	II	III	
Control object	1.24	0.26	0.32	0.61
100kg N (sludge)	1.06	0.37	0.35	0.59
150kg N (sludge)	1.01	0.32	0.27	0.53
200kg N (sludge)	1.22	0.30	0.37	0.63
150kg N (urea)	0.99	0.36	0.30	0.55
Mean	1.10	0.32	0.33	0.58

The content of investigated elements determined in willow biomass in own research was contained in a range of papers published by others authors [13, 14]. Results presented in this paper related to phosphorus indicated on the lower degree of phosphorus availability for willow from sewage sludge that from mineral fertilizer mainly in the second and third year of cultivation. The lower content of sulfur determined in willow biomass harvested from plots fertilized with lower doses of sewage sludge than that from object with mineral fertilizer as well as in comparison with the sulfur content in others energetic materials [12] indicates that the pollution of environment should be lower when biomass of willow harvested from plots fertilized with sewage sludge will be used as energetic materials.

Conclusions

In the field experiment carried out during three years with the fertilization of willow (*Salix viminalis*) in which biomass was harvested every year by different doses of sewage sludge on the loamy light sandy soil the following conclusions were drawn out:

1. The content of all determinated P, K, S, Ca, Mg and Na elements were significantly differentiated upon the year of harvesting. The highest content of P, K and S were determinated in willow biomass harvested in the first, whereas Ca, Mg and Na in the second year of cultivation.
2. The highest content of all determinated elements was stated in biomass harvested from plots fertilized with mineral fertilizers (urea).
3. The highest content of all determinated elements contained the biomass harvested from plots fertilized with the highest dose from plots fertilized with the highest dose of sewage sludge (200 kg · ha^{-1} of N) and the lowest with plots fertilized with sewage sludge in the middle dose (150 kg · ha^{-1} of N).
4. Uptake by willow biomass of Ca, Mg, S and Na was the highest in the second year, whereas the P and K increase in the following years of cultivation.
5. The value of relation of chemical elements one- to bivalent (K + Na)/(Ca + Mg) in small degree were diverse in dependence from applied fertilization, however they were clearly larger in first year of the willow cultivation than in second and third.

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WPŁYW DAWEK AZOTU ZASTOSOWANEGO W OSADZIE ODCIEKOWYM NA ZAWARTOŚĆ MAKROELEMENTÓW W WIERZBIE (*Salix viminalis*)

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Abstrakt: Określono wpływ zróżnicowanych dawek azotu wprowadzonych do gleby w osadach ściekowych oraz nawożenia mineralnego na zawartość i pobranie fosforu, potasu, siarki, wapnia, magnezu i sodu przez wierzbę krzewiastą (*Salix viminalis*). W doświadczeniu polowym uprawiano wierzbę na obiektach nawożonych osadami ściekowymi w dawkach odpowiadających wprowadzeniu do gleby 100, 150, i 200 kg N · ha^{-1}. Ponadto wydzielono obiekt nawożony corocznie przez 3 lata mocznikiem w dawce 50 kg N · ha^{-1}, co w sumie stanowiło 150 kg N. Zawartość badanych pierwiastków w pędach wierzby na ogół nie była istotnie uzależniona od dawki osadu ściekowego. Tylko zawartość potasu i siarki w uzyskanej biomasie była istotnie największa po zastosowaniu największej dawki osadu. Zawartość potasu, siarki, wapnia, magnezu i sodu w pędach wierzby nawożonej osadami ściekowymi i NPK w postaci mineralnej najczęściej nie różniła się istotnie, natomiast zawartość fosforu była istotnie mniejsza po zastosowaniu osadów niż nawożenia mineralnego. Najwięcej badanych pierwiastków (potasu, siarki, wapnia i magnezu) rośliny wierzby pobrały w II roku uprawy, a najmniej w I roku po założeniu plantacji. Pobranie fosforu zwiększało się w kolejnych latach uprawy wierzby.

Słowa kluczowe: osady ściekowe, azot, wierzba, makroelementy

DOI: 10.2428/ecea.2012.19(04)039 ECOL CHEM ENG A. 2012;19(4-5):377-385

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CONTENT AND AMOUNTS OF CADMIUM AND LEAD UPTAKEN BY SPRING WHEAT BIOMASS AFTER FERTILIZATION WITH SEWAGE SLUDGE

ZAWARTOŚĆ I ILOŚCI KADMU I OŁOWIU POBRANE PRZEZ BIOMASĘ PSZENICY JAREJ PO NAWOŻENIU OSADAMI ŚCIEKOWYMI

Abstract: Despite numerous experiments testing potential management of biodegradable wastes including municipal sewage sludge, their practical application is still unsatisfactory. The problem of rational, but principally safe utilization of these waste materials is still an open and widely discussed issue. Fertilizer value of municipal sewage sludge, which have been emphasized on many occasions seem insufficient grounds to encourage farmers to use materials of this type to fertilize soils and enrich plants. The experiment aimed to assess cadmium and lead contents and the amounts of these elements absorbed by spring wheat biomass after its fertilization with municipal sewage sludge. The research was conducted as a three-year field experiment on stagnic gleysol with granulometric composition of heavy silt loam.

Mean weighted cadmium content in spring wheat biomass was significantly the highest after the application of exclusively mineral fertilizers and municipal sewage sludge from mechanical-biological treatment plant. The greatest amounts of lead were assessed in wheat grain from the treatment where farmyard manure was used. While for straw a non-proven tendency for greater accumulation of this element on treatments receiving farmyard manure and sewage sludge from mechanical-biological treatments plant was assessed. Regardless of the fertilization, spring wheat accumulated greater amounts of cadmium and lead in straw than in grain. The contents of both analyzed heavy metals met the criteria of permissible contents in grain destined for animal feed (to 1.00 mg Cd or 10 mg Pb $\cdot$ kg^{-1} d.m.).

Keywords: cadmium, lead, spring wheat, sewage sludge

Introduction

Despite numerous experiments testing potential management of biodegradable materials, including municipal sludge, their practical application remains unsatisfactory. The problem of rational and principally safe utilization of these waste materials is still an open and widely discussed issue. Frequently emphasized fertilizer values of

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municipal sewage sludge seem to be insufficient argument encouraging farmers to use this type of materials to fertilize soils and plants [1–4].

Impurities contained in sewage sludge, including heavy metals such as cadmium or lead may cumulate in plants, worsening their quality [5, 6]. The contents of toxic heavy metals in plants requires monitoring because their potentially dangerous levels (showing no symptoms of harmful effect on plants) may be reached in plant diet of both animals and humans [7].

The experiment was conducted to assess the contents and amounts of cadmium and lead taken up by spring wheat biomass after its fertilization with municipal sewage sludge.

Material and methods

The assessment of applied fertilization effect on the contents and amounts of cadmium and lead absorbed by spring wheat biomass was carried out in the years 2005–2007 as a field experiment on arable land localized 10 km west of Krakow (49°59,625′ N; 19°41,910′E). The soil from the experimental area was classified as Stagnic Gleysol soil with granulometric composition of heavy silt loam. Basic soil properties prior to the research outset were determined using usual agricultural chemistry methods [8] and were presented in Table 1.

Table 1

Some properties of farmyard manure, sewage sludge and soil before establishment of experiment

Determination		FYM	SSI	SSII	Soil
Dry matter $[g \cdot kg^{-1}]$		226	297	258	—
pH H_2O		8.23	6.23	6.57	5.94
Total N	$[g \cdot kg^{-1}$ d.m.]	34.0	26.2	41.6	1.59
Total P		12.8	8.2	22.3	—
Total K		21.8	1.92	1.26	—
Available P	$[mg \cdot kg^{-1}$ d.m.]	—	—	—	72
Available K		—	—	—	298
Total Cd		0.80	3.97	1.86	0.96
Total Pb		1.18	55.74	12.88	35.80
Total Cu		156	104	81	15.81
Total Cr		2.84	23.36	18.38	51.61
Total Zn		284	1146	950	133
Total Ni		10.10	21.09	9.38	32.74
Total Hg		0.11	0.20	0.10	0.90

The experiment was set up using randomized block method. The fertilized plot area was 30 m^2 (5 m · 6 m). The experimental design comprised 5 treatments in four replications:

– soil without fertilizers (0),

– soil fertilized with mineral fertilizers (NPK),

– soil fertilized with swine manure (FYM),

– soil fertilized with municipal sewage sludge from mechanical-biological treatment plant in Krzeszowice (SSI),

– soil fertilized with municipal sewage sludge from biological treatment plant in Czernichow (SSII).

The sewage sludge and manure were applied once in the first year of the experiment. Basic chemical properties were assessed in the manure and sewage sludge [9] and the obtained results were shown in Table 1.

Before the experiment started the soil was limed according to value of hydrolytic acidity. The following spring, following the basic cultivation measures, manure and municipal sewage sludge were spread on the plots surfaces and ploughed (to the depth of 20 cm). Two weeks later mineral fertilizers were applied on NPK treatment and supplementary mineral fertilization (P, K) on the treatments where previously manure and sewage sludge were used. The fertilizers were mixed with the soil using a field cultivator with harrow. Nitrogen dose supplied with the fertilizers was 110.0 kg $N \cdot ha^{-1}$. Phosphorus and potassium were supplemented to equal level introduced with fertilization on all treatments (except the control), phosphorus to 58.6 kg $P \cdot ha^{-1}$ as single superphosphate and potassium to 120.0 kg $K \cdot ha^{-1}$ as 60 % potassium salt. On the treatment where mineral fertilizers were used, nitrogen was applied as ammonium nitrate.

In order to avoid species changeability in the conditions of conducted experiments, each year the test plant was spring wheat, 'Jagna' c.v. The assumed plant density was 485 plants per 1 m^2. In the second and third year of the investigations, identical as in the first year doses were applied to supplement the nutrients (N, P and K) but exclusively in the form of mineral fertilizers. The length of wheat vegetation period depended on the weather conditions and was 117 days in the first, 106 in the second and 107 days in the third year. Wheat was harvested at full maturity. Chemical plant protection measures were applied during the vegetation period to protect the plantation against weeds and fungal diseases. In order to determine wheat grain yield in field conditions the plants were harvested from 4 m^2 area, from each plot separately. After ear threshing the obtained grain and straw yields were dried (at 70 ^oC) and dry mass content was determined. In dried and ground plant material cadmium and lead contents were assessed after sample dry mineralization in a chamber furnace (450 ^oC, 5 hrs.) and dissolving the remains in a diluted (1:2) nitric acid [10]. The studied elements concentrations were assessed in the prepared solutions using ICP-AES method on JY 238 Ultrace apparatus.

Chemical analysis was conducted on the experimental material in four replications and on initial materials (manure, sewage sludge, soil) in two replications. A plant reference material sample – NCS DC733448 (China National Analysis Center for Iron & Steel) was added to each analyzed series.

One way ANOVA was conducted for the obtained results in totally randomized design using f-Fisher test. The significance of differences between the arithmetic means was verified on the basis of homogenous groups determined by means of t-Tukey test at the significance level $p < 0.05$. All statistical computations and graphical presentations of the results were made using Statistica PL packet [11].

The meteorological conditions (precipitations and temperature) during the experiment were presented in Tables 2 and 3.

Table 2

Monthly and periodic precipitation totals in study years [mm]

Year	Month						Σ January–December
	March	April	May	June	July	August	
2005	20.7	49.1	61.3	40.6	113.4	102.6	597.5
2006	60.1	56.5	51.9	89.1	14.1	104.1	567.9
2007	61.1	15.4	51.7	72.1	71.0	76.4	830.4

Table 3

Mean daily air temperature in study years [^{o}C]

Year	Month						Mean January–December
	March	April	May	June	July	August	
2005	–0.2	6.8	11.4	14.4	17.6	15.4	6.8
2006	0.2	5.6	10.9	15.0	18.6	15.6	7.5
2007	6.0	8.5	15.2	18.4	19.4	19.0	9.2

The weather conditions during the experiment period differed, particularly between the years. The highest precipitation amount during the plant growing period (total from March to August) was characteristic for the year 2005 (1st year of the experiment). The year 2007 was characterized by a higher mean annual temperature, whereas mean temperature during the spring wheat vegetation period (March to August) generally did not differ.

Results and discussion

The yields of spring wheat grain in the first year of the investigations harvested from the treatments where manure (FYM) and municipal sewage sludge from biological treatment plant (SSII) were applied were by 0.70 Mg (ton) d.m. $\cdot$ ha^{-1} lower in comparison with the wheat grain yield fertilized with mineral fertilizers (NPK). 0.30 Mg (ton) d.m. $\cdot$ ha^{-1} less of wheat grain, as compared with wheat grain fertilized with mineral fertilizers (NPK) was gathered on the treatment where sewage sludge from mechanical-biological treatment plant was used (Fig. 1). However, statistical analysis conducted for the results did not confirm the significance of differences. In the second year of the research, the lowest grain yield among the fertilized treatments was harvested from the manure treatment (FYM) (Fig. 1). On the treatments where

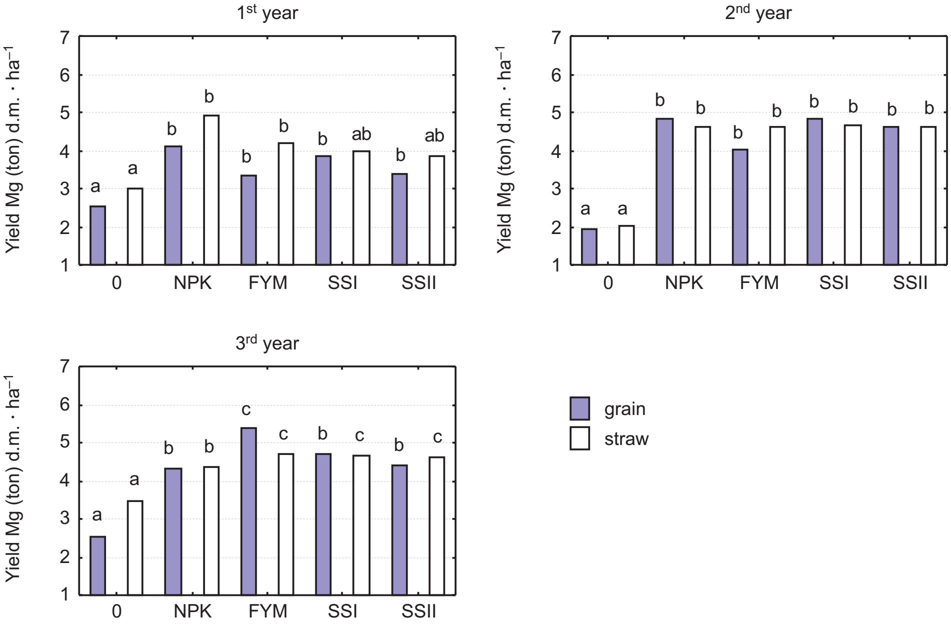

Fig. 1. Grain and straw yields of spring; Means followed by the same letters did not differ significantly at $p < 0.05$ according to the Tukey test

municipal sewage sludge was used as fertilizer, spring wheat grain yields were approximate or identical to those gathered from mineral fertilizers (NPK) treatment.

In the third year of the investigations on treatments receiving organic materials spring wheat grain yield was bigger than harvested from the treatment where only mineral fertilization (NPK) was used, still statistically proved increase in yield was registered only on the treatment where farmyard manure (FYM) was applied (Fig. 1).

Slightly greater diversification charcterized straw yields, particularly in the first year of the experiment (Fig. 1). Mineral fertilization (NPK) definitely best affected the yields of this plant part. On the treatments where manure fertilization (FYM) and municipal sewage sludge were used (SSI, SSII) straw yields were similar (3.9; 4.2) Mg (ton) d.m. · ha^{-1}. In the second year of the research applied fertilization did not cause any notable changes in the quantities of straw biomass gathered from individual treatments. Significantly better effect of fertilization with manure and municipal sewage sludge on the amount of spring wheat straw biomass in comparison with mineral fertilizer effect, was observed in the third year of the experiment. Increases in straw biomass amount on these treatments, as compared with the straw quantity harvested on the treatment where mineral fertilizers were used were respectively: 6.8 % (FYM); 6.8 % (SSI) and 4.5 % (SSII).

The obtained results indicate a lesser direct yield forming effectiveness (in the first year after application) of fertilization with both municipal sewage sludge and farmyard manure as compared with mineral fertilizers. Lower yields of wheat grain and straw in the first year of research on treatments where municipal sewage sludge and manure were used resulted from more difficult plant access mainly to nitrogen present in the applied materials, primarily as organic combinations. The causes of this situation should be sought in a relatively short period of time (spring), during which applied organic materials were undergoing mineralization process in soil. A beneficial result of the consequent effect of municipal sewage sludge on wheat yields were registered in the third year of the investigations. Only the consequent effect of farmyard manure fertilization proved significant both in case of wheat straw and grain. A significant consequent effect of plant fertilization with organic materials was not corroborated by the research results of Woloszyk [12] and Skowronska et al [13]. According to Sienkiewicz [14] farmyard manure fertilizer effect on wheat grain yield was significant in relation to mineral fertilizers effect, although the author emphasizes that the fertilization was not equally efficient over the three-year period of investigations. Moreover, Sienkiewicz [14] noticed that a lower effectiveness of farmyard manure should be sought in the unfavourable weather conditions, *eg* excessive rainfall.

Cadmium is not a crucial element for the growth and development to plants. Due to its considerable mobility in soil it is easily absorbed by plants. Mean weighted average cadmium content for three years, both in the spring wheat grain and straw was significantly highest in the biomass from the treatments fertilized exclusively with mineral fertilizers (NPK) and from the treatment where wheat was fertilized with municipal sewage sludge from the mechanical-biological treatment plant (SSI) (Table 4).

Table 4

Content of cadmium and lead in biomass of spring wheat [$mg \cdot kg^{-1}$ d.m. ± SD; n = 4]; weighted mean from three years

Fertilization	Cd		Pb	
	grain	straw	grain	straw
0	$0.17^{a} \pm 0.03$	$0.24^{a} \pm 0.05$	$0.23^{a} \pm 0.05$	$0.62^{a} \pm 0.04$
NPK	$0.26^{b} \pm 0.04$	$0.38^{b} \pm 0.10$	$0.20^{a} \pm 0.03$	$0.60^{a} \pm 0.05$
FYM	$0.18^{a} \pm 0.04$	$0.27^{a} \pm 0.09$	$0.31^{b} \pm 0.03$	$0.68^{a} \pm 0.08$
SSI	$0.23^{b} \pm 0.02$	$0.32^{b} \pm 0.03$	$0.20^{a} \pm 0.03$	$0.69^{a} \pm 0.12$
SSII	$0.17^{a} \pm 0.04$	$0.27^{a} \pm 0.06$	$0.16^{a} \pm 0.03$	$0.64^{a} \pm 0.09$

Means followed by the same letters in columns did not differ significantly at $p < 0.05$ according to the Tukey test.

Mean weighted average content of this element in the biomass from the treatments where manure (FYM) and municipal sewage sludge from biological treatment plant (SSII) were applied remained on the level assessed in wheat biomass from the control (0) treatment. Mean weighted average cadmium content in wheat grain, irrespective of the fertilization used, did not exceed the critical value (1 $mg \cdot kg^{-1}$ d.m.) classifying the biomass for fodder [15].

The largest cadmium amounts taken up by spring wheat biomass were assessed on the treatments receiving exclusively mineral fertilizers (NPK) and municipal sewage sludge from mechanical-biological treatment plant (SSII) (Table 5).

Table 5

Uptake of cadmium and lead with biomass of spring wheat [$g \cdot ha^{-1} \pm SD; n = 4$] in period three years

Fertilization	Cd		Pb	
	grain	straw	grain	straw
0	$1.16^{a} \pm 0.17$	$2.09^{a} \pm 0.52$	$1.64^{a} \pm 0.34$	$5.24^{a} \pm 0.37$
NPK	$3.51^{d} \pm 0.68$	$5.27^{b} \pm 1.56$	$2.70^{b} \pm 0.34$	$8.33^{b} \pm 0.84$
FYM	$2.29^{bc} \pm 0.59$	$3.67^{ab} \pm 1.34$	$4.02^{c} \pm 0.49$	$9.26^{b} \pm 1.04$
SSI	$3.12^{d} \pm 0.12$	$4.29^{b} \pm 0.41$	$2.62^{b} \pm 0.44$	$9.14^{b} \pm 1.36$
SSII	$2.01^{ab} \pm 0.20$	$3.50^{ab} \pm 0.50$	$1.91^{ab} \pm 0.10$	$8.38^{b} \pm 0.81$

Means followed by the same letters in columns did not differ significantly at $p < 0.05$ according to the Tukey test.

Relatively small quantity of cadmium supplied to the soil with applied fertilizers was not the only factor affecting this element content in spring wheat biomass. Also soil properties, particularly its pH played an important role [16]. The fact was confirmed by the highest weighted average cadmium contents in wheat biomass on the mineral fertilizers treatment (where the soil pH values were the lowest) in comparison with these elements contents assessed in the grain and straw from the treatments fertilized with municipal sewage sludge and farmyard manure. Cadmium contents assessed in wheat grain irrespectively of the applied fertilization were obviously smaller than the concentrations determined by Renoux et al [17] in barley fertilized with sewage sludge. On the other hand, Wisniowska-Kielian and Klima [18] found much smaller contents of cadmium in grain of winter wheat forms originating from both organic and conventional cultivation. However, in the research conducted by the authors mentioned above soil contents of cadmium were notably lower. It might have significantly affected the content of this element bioavailable forms and in result also Cd content in the analyzed biomass. A marked dependence between Cd content in soil and its plant concentrations was confirmed by the results of research of Chaudri et al [19] and Adams et al [20].

Like cadmium, lead is not the element necessary for plant growth and development and its concentrations in the biomass are conditioned among others by the concentrations of its bioavailable forms in the soil solution. Mean weighted average content of lead in wheat grain ranged widely, irrespectively of the applied fertilization (from 0.16 to 0.31 $mg \cdot kg^{-1}$ d.m.) (Table 4). The biggest amounts of lead were assessed in wheat grain fertilized with manure (FYM), whereas the smallest in wheat grain from the treatment where municipal sewage sludge from biological treatment plant (SSII) was applied. The content was comparable with the values determined in grain from treatments receiving exclusively mineral fertilizers (NPK) and sewage sludge from the mechanical-biological treatment plant (SSI). Spring wheat straw contained between 2 and 4 times higher amounts of lead than grain, irrespective of applied fertilization (Table 4).

Quantities of lead taken up by spring wheat biomass were diversified mainly with respect to yield of the analyzed plant parts (Table 5). Wheat plants absorbed much higher amounts of lead with straw. Independently of the plant part, wheat absorbed the highest amounts of lead on the treatment where manure (FYM) was used.

The main role in processes affecting lead ions activity in soil solution has been ascribed to clay minerals and organic substance [7, 21]. On the basis of its granulometric composition, the soil from the experimental area was classified to agronomic category of heavy soils, which significantly limited lead availability to plants. Lead contents assessed in spring wheat grain, irrespectively of applied fertilizers, were higher than determined by Wisniowska-Kielian and Klima [18] in grain of winter wheat forms from organic and conventional cultivation or assessed by Bednarek et al [22]. Still, these contents did not limit the grain use for animal feed [15].

Conclusions

1. Mean weighted cadmium content in spring wheat biomass was significantly highest after the application of exclusively mineral fertilization and municipal sewage sludge from mechanical-biological treatment plant.
2. Wheat grain from the treatment receiving swine manure contained the largest lead concentrations, whereas a non-proven tendency for greater accumulation of this element was observed on treatments with farmyard manure and sewage sludge from mechanical--biological treatment plant.
3. Spring wheat accumulated bigger quantities of cadmium and lead in straw than in grain, independently on the applied fertilizers.
4. The contents of both analyzed heavy metals fulfilled the criteria of these elements permissible contents in grain destined for animal forage (to 1.00 mg Cd and 10 mg Pb $\cdot$ kg^{-1} d.m.

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ZAWARTOŚĆ I ILOŚCI KADMU I OŁOWIU POBRANE PRZEZ BIOMASĘ PSZENICY JAREJ PO NAWOŻENIU OSADAMI ŚCIEKOWYMI

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Abstrakt: Pomimo wielu badań dotyczących możliwości zagospodarowania odpadów ulegających biodegradacji, w tym komunalnych osadów ściekowych, ich praktyczne wykorzystanie jest niezadowalające. Problem racjonalnego, a przede wszystkim bezpiecznego wykorzystania tych materiałów odpadowych jest nadal otwarty i szeroko dyskutowany. Wielokrotnie podkreślane walory nawozowe komunalnych osadów ściekowych wydają się być niewystarczającym argumentem zachęcającym rolników do stosowania tego rodzaju materiałów odpadowych w celu użyźniania gleb i nawożenia roślin. Celem przeprowadzonych badań była ocena zawartości kadmu i ołowiu oraz ilości tych pierwiastków pobranych przez biomasę pszenicy jarej po nawożeniu komunalnymi osadami ściekowymi. Badania przeprowadzono w 3-letnim doświadczeniu polowym na glebie opadowo-glejowej o składzie granulometrycznym gliny ciężkiej pylastej.

Średnia ważona zawartość kadmu w biomasie pszenicy jarej była istotnie największa po zastosowaniu wyłącznie nawożenia mineralnego oraz komunalnego osadu ściekowego pochodzącego z oczyszczalni mechaniczno-biologicznej. Najwięcej ołowiu zawierało ziarno pszenicy z obiektu, w którym stosowano obornik, a w przypadku słomy wystąpiła nieudowodniona tendencja do większego nagromadzenia tego pierwiastka w obiektach z obornikiem i osadem ściekowy z oczyszczalni mechaniczno-biologicznej. Więcej kadmu i ołowiu pszenica jara akumulowała w słomie niż w ziarnie, niezależnie od zastosowanego nawożenia. Zawartości obydwu badanych metali ciężkich spełniała kryteria dopuszczalnych zawartości w ziarnie przeznaczonym na cele paszowe (do 1,00 mg Cd lub 10 mg Pb $\cdot$ kg^{-1} s.m.).

Słowa kluczowe: kadm, ołów, pszenica jara, osady ściekowe

DOI: 10.2428/ecea.2012.19(04)040 ECOL CHEM ENG A. 2012;19(4-5):387-393

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POST-EFFECT OF BOTTOM SEDIMENT ADDITION TO THE SUBSTRATUM ON CHEMICAL COMPOSITION OF WHITE MUSTARD (*Sinapis alba* L.) BIOMASS

Part 2. QUANTITATIVE RATIOS BETWEEN MACROELEMENTS*

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

Cz. 2. STOSUNKI ILOŚCIOWE MIĘDZY MAKROELEMENTAMI*

Abstract: The aim of the work was an assessment of a bottom sediment supplement to the substratum on the composition of plant biomass determined on the basis of quantitative relationships between macroelements. The experiment was a continuation of previous research conducted in 2005 and 2006, when the test plants were: Italian ryegrass (*Lolium multiflorum* L.) and maize (*Zea mays* L.), respectively. The quality of white mustard (*Sinapis alba* L.) shoot biomass cultivated in the third year after the application of bottom sediment dredged from the Roznow Reservoir was assessed. The sediment was added to the soil in quantities constituting between 1 and 20 % of the substratum mass. Macroelement content was determined in the obtained material and subsequently weight ratios Ca : P, Ca : Mg, K : Ca, K : Mg and K : Na, as well as K : (Ca + Mg) ionic ratio were computed.

A considerable diversification of relationships between macroelements was revealed in mustard shoot biomass growing on substrata with diverse share of bottom sediment. In white mustard biomass from the control treatment (soil without sediment addition) K:Ca ratio assumed a value close to optimal, Ca : P, K : Mg and K : Na ratios were about 3-fold higher, Ca : Mg was 4-fold higher than optimal, whereas K : (Ca + Mg) ratio was over twice lower than optimal. Increasing share of the sediment in the substratum generally caused a widening of Ca : P ratio and narrowing of K : Ca, K : Mg, K : Na, Ca : Mg and K : (Ca + Mg) ratios in mustard biomass. The changes led to a serious worsening of Ca : P, K : Ca and K : (Ca + Mg) ratios in mustard biomass but caused a marked improvement of K : Mg and K : Na ratios bringing them close to the optimum. They also bettered Ca : Mg ratio but did not lead it to the optimal value. The reason of worsening Ca : P, K : Ca and K : (Ca + Mg) ratios was a large Ca content in plant biomass resulting from a relatively high its content in bottom sediment despite applied NPK mineral fertilization and the antagonism among the

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* Part I: Ecol Chem Eng A. 2011;18(9-10):1175-1184.

elements. The cause of modification of the relationships between the elements may be changes of the substratum pH resulting from bottom sediment addition to the soil, particularly in the range of between 3 to 20 % which induced a raise in pH value, proportional to the sediment share in the substratum. The highest sediment admixtures led the substratum pH to approximate neutral.

Bottom sediment dredged from the Roznow Reservoir may be used for improvement of light acid soil properties, but it may cause a worsening of the weight ratios between calcium and other macroelements, particularly P and K.

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

Fodder plant production makes use of fertilizers which affect chemical composition of plants and nutrient resources in soil. Qualitative and quantitative changes of mineral elements occurrence in plants are determined by such factors as the species and development stage of a plant, the weather changing during their growth and development as well as soil properties. Therefore, it is necessary to assess plant chemical composition, also with reference to mineral components [1].

Macroelement content in fodder and proper ratios between them condition animal health. As reported by Czuba and Mazur [2] optimal ratios between individual elements should be as follows: Ca : P = 2 : 1, Ca : Mg = 2 – 3 : 1, K : Mg = 6 : 1, K : Ca = 2 : 1 and K : Na = (5–8) : 1. The quality indicator used for the assessment of plant nutritional value of ruminant feed K :(Ca + Mg) should be 1.62 but may not exceed 2.2 [3].

The aim of the investigations was an assessment of post-effect of bottom sediment additions to the substratum on the quantitative ratios between essential macroelements in obtained plant biomass and indirectly the estimation of possibility of agricultural application of this sediment.

Material and methods

The researched material was shoot biomass of white mustard (*Sinapis alba* L.) cultivated in pot experiment in the third year after the bottom sediment, dredged from the Roznow Reservoir, application to very light and very acid soil. The experiment continued the research conducted in 2005 and 2006 on test plants, first Italian ryegrass (*Lolium multiflorum* L.) and then maize (*Zea mays* L.).

Before the experiment, the sediment and soil were air-dried, crushed mechanically and sifted and then their essential properties and bioavailable forms of P and K were determined (Table 1 and 2).

Table 1

The basic properties of components of the substrate

Component	pH		Hh	C_{org}	N_{tot}	Bioavailable	
						P_2O_5	K_2O
	KCl	H_2O	[$mmol^{(+)} \cdot kg^{-1}$]	[$g \cdot kg^{-1}$]		[$mg \cdot kg^{-1}$]	
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

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

Bottom sediment was added to the soil in the amounts constituting between 1 and 20 % of the substratum mass, whereas the control treatment was light, very acid soil without the sediment addition (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

After harvesting mustard shoot biomass was dried and ground, and in the material prepared in this way macroelement content was determined by means of AAS and ICP-AES methods after previous dry mineralization and ash dissolving in HNO_3 (3:1, v/v). On the basis of macroelements content the reciprocal quantitative ratios between them were calculated.

Results and discussion

The contents of analyzed macroelements in the aboveground mustard biomass were assessed in the following ranges: (36.8–47.1) g N, (2.25–5.20) g P, (7.52–47.47) g K, (26.26–42.50) g Ca, (2.3–4.5) g Mg and (1.11–4.67) g Na in 1 kg of dry mass [4].

The quality of plant material is determined not only by the absolute element content but also by the quantitative relationships between them. Many authors point to the ratios between elements in plants due to various interactions between them, which may causes element deficiencies, even when their contents are regarded as adequate [1, 5, 6]. The quality of obtained plant biomass was determined on the basis of quantitative ratios between mineral elements content in aboveground parts of white mustard. The most frequently assessed are weight ratios: Ca : P, Ca : Mg, K : Ca, K : Mg and K : Na as well as ionic ratio K : (Ca + Mg).

Value of weight Ca : P ratio in good quality plant material should be 2 : 1 [1]. In biomass of mustard obtained on the soil without the sediment supplement, the ratio was almost thrice higher than the optimal (Fig. 1). Subsequent additions of the sediment led to further widening of this ratio, from 3.6 to about 6 times larger in comparison with the optimal value.

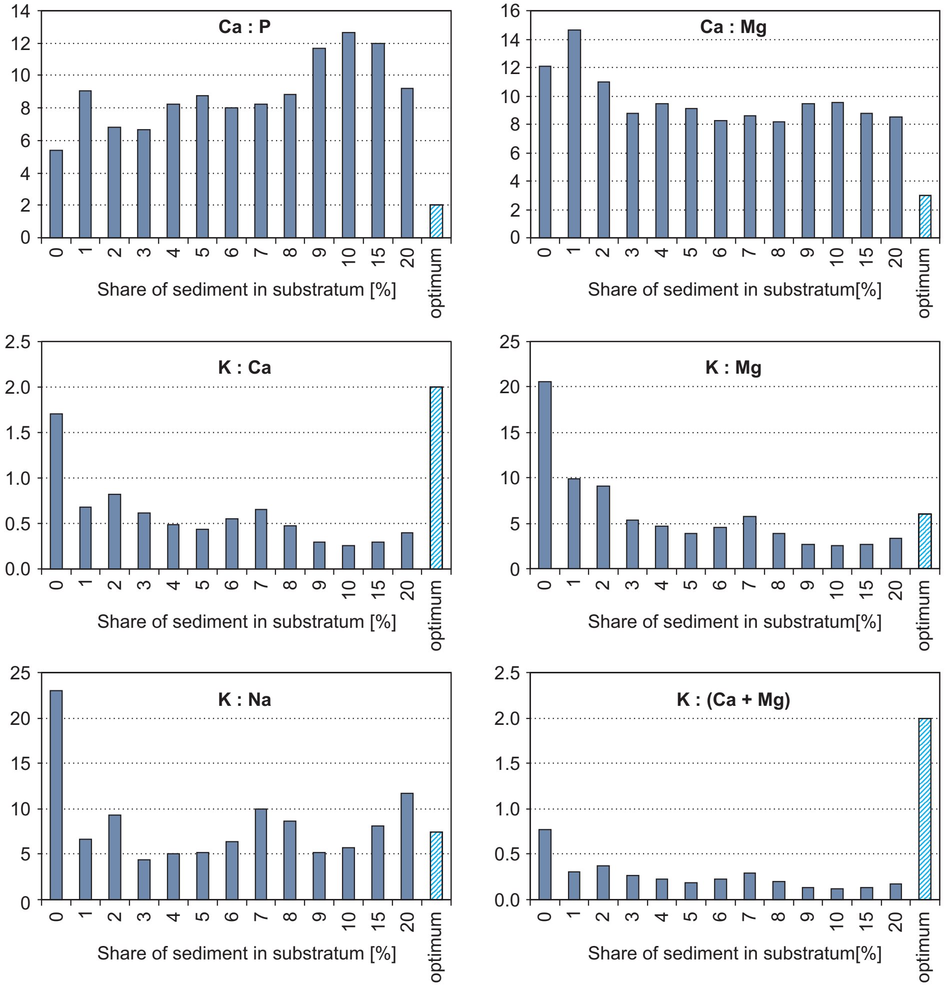

Fig. 1. Values of reciprocal ratios between individual elements in the aboveground biomass of mustard depending on the share of sediment in the substratum

Mustard revealed a disadvantageous value of Ca : Mg weight ratio, because the right one should be 3 : 1 [5] (Fig. 1). Weight Ca : Mg ratio in mustard biomass from all studied treatments exceeded the optimal value between 2.5 and 5-fold. The least difference in relation to the optimal value might be observed in the plants grown in treatment with 8 % share of the sediment in the substratum and the greatest when sediment share amounted 1 %.

K : Ca weight ratio in the analyzed plant biomass assumed too low values (Fig. 1). Only on the soil without the sediment supplement this ratio was close to optimal, *ie* 2 : 1, whereas successive sediment additions caused its narrowing and then it assumed the values between 2.5 to 10-fold smaller than optimum.

In shoot biomass of mustard grown in the control and in the treatment with the smallest sediment additions to the substratum (1; 2) % K content in relation to Mg was excessive (Fig. 1). In mustard grown on treatments with 3 and 7 % suplements of bottom sediment to the substratum K:Mg weight ratio was 6:1, *ie* close to optimal. In plant material from the other treatments the ratio had value between about 30 and 60 % lower than optimal.

K : Na weight ratio in good quality plant material should be (5–8) : 1 [1, 5]. In about 60 % of samples the ratio had value approximate to optimal. In about 40 % samples K : Na ratio indicated an excessive K content in relation to Na (Fig. 1), therefore it was by 30 % to 300 % higher than optimal.

K : (Ca + Mg) ratio in good quality plant material should be 2 : 1 [1]. In this respect mustard shoot biomass revealed unsatisfactory quality (Fig. 1). The highest value of this ratio was observed in the control plants, however it was about twice lower than the optimal. K : (Ca + Mg) ratio assumed the lowest value when sediment share in the substratum amounted 10 % and it was about 17-fold lower than the optimal value of this ratio.

Too big prevalence of calcium over phosphorus, potassium and magnesium in the assessed plant material may be explained by the fact that the sediment already contained considerable amounts of this element, *ie* 17.46 $\mathrm{gCa \cdot kg^{-1}}$. Lower content of K in relation to Ca and Mg may be explained by the antagonism of these elements. Sediments from dam reservoirs as well as from lakes are characterized by a great share of silt and clay fractions in their granulometric composition, reaching around 50 % each [7, 8], relatively high pH values, corresponding to neutral reaction [9], and high calcium content, up to 125.93 $\mathrm{gCa \cdot kg^{-1}}$ d.m., even in case of pH lower than 6.5 [10]. In Authors own studies addition of bottom sediment to the soil caused changes of reaction depending on its share in the substratum (Fig. 2).

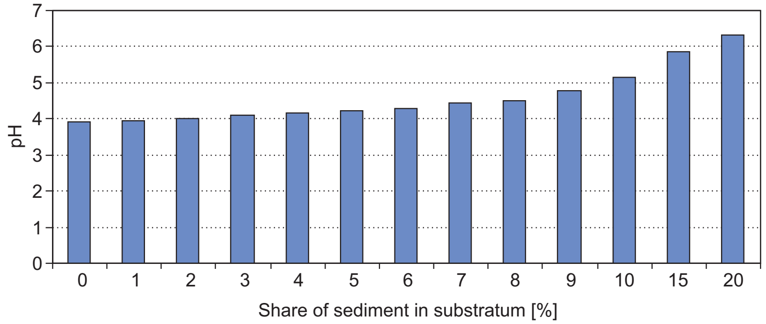

Fig. 2. pH value of substratum after white mustard harvest depending on a share of bottom sediment

An addition of 1 and 2 % of the sediment did not bring about any visible changes of the soil reaction, only bigger supplements, from 3 to 20 % caused a linear growth of pH value, proportionally to the amount of added sediment. Application of the highest additions of the sediment brought the substratum reaction to almost neutral.

Quantitative ratios between the macroelements in most cases were improper. Niemiec [11] obtained similar interrelationships in his research on potential environmental applications of bottom sediment. An addition of bottom sediment improved K : Mg and K : Na ratio, but worsened calcium relation to other macroelements. Causes of these dependencies should be sought in relatively high calcium contents in the used sediment.

Conclusions

1. In mustard biomass from the control treatment (soil without bottom sediment addition) only K : Ca weight ratio approximated the optimal value, Ca : P, K : Mg and K : Na weight ratios assumed thrice higher values, Ca : Mg was four-fold higher than optimal, whereas K : (Ca + Mg) ionic ratio was over twice lower than the optimum.
2. Increasing share of sediment in the substratum generally caused a widening of Ca : P ratio and narrowing of K : Ca, K : Mg, K : Na, Ca : Mg and K : (Ca + Mg) ratios in mustard aboveground biomass. The changes led to a considerable worsening of Ca : P, K : Ca and K : (Ca + Mg) ratios and to an apparent improvement of K : Mg and K : Na ratios approximating them to the optimum. They also improved Ca : Mg ratio but did not bring this relationship to the optimal value.
3. The reason for worsening of Ca : P, K : Ca and K : (Ca + Mg) ratios was an excessive Ca content in the plant biomass resulting from a relatively high Ca amount in bottom sediment, despite the applied mineral NPK fertilization and the antagonism between the elements.
4. The cause of modification of the rations between the macroelements may be changes of the substratum reaction due to an addition of bottom sediment to the soil, particularly within the (3–20) % range, which caused an increase in pH value, proportional to the sediment share in the substratum. The highest sediment additions approximated the substratum pH almost to neutral.
5. Bottom sediment dredged from the Roznow Reservoir may be used for improvement of light acid soil properties, however, it may cause worsening of weigh rations between calcium and the other macroelements, particularly P and K.

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

Cz. 2. STOSUNKI ILOŚCIOWE MIĘDZY MAKROELEMENTAMI

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Abstrakt: Celem pracy była ocena oddziaływania dodatku osadu dennego do podłoża na skład biomasy roślinnej ocenianej na podstawie stosunków ilościowych między makroelementami. Badania były kontynuacją doświadczeń prowadzonych w latach 2005 i 2006, w których roślinami testowymi były kolejno życica wielokwiatowa (*Lolium multiflorum* L.) i kukurydza (*Zea mays* L.). Oceniano jakość nadziemnej biomasy gorczycy białej *(Sinapis alba* L.), uprawianej w trzecim roku po zastosowaniu osadu dennego bagrowanego ze Zbiornika Rożnowskiego. Osad dodawano do gleby w ilości od 1 do 20% masy podłoża. W uzyskanym materiale roślinnym oznaczono zawartość makroelementów, a następnie obliczono stosunki masowe Ca : P, Ca : Mg, K : Ca, K : Mg i K : Na oraz stosunek jonowy K : (Ca + Mg).

Wykazano znaczne zróżnicowanie stosunków między makroelementami w nadziemnej biomasie gorczycy rosnącej na podłożach ze zwiększającym się udziałem osadu dennego. W biomasie gorczycy białej z obiektu kontrolnego (gleba bez dodatku osadu dennego) stosunek K : Ca przyjmował wartość bliską optymalnej, stosunki Ca : P, K : Mg i K : Na – około 3-krotnie wyższe, a Ca : Mg – 4-krotnie wyższy niż optymalne, natomiast stosunek K : (Ca + Mg) miał wartość ponad 2-krotnie niższą od optymalnej. Wzrastający udział osadu w podłożu powodował na ogół rozszerzenie stosunku Ca : P oraz zacieśnienie stosunków K : Ca, K : Mg, K : Na, Ca : Mg i K : (Ca + Mg) w biomasie gorczycy. Zmiany te prowadziły do znacznego pogorszenia stosunków Ca : P, K : Ca i K : (Ca + Mg) w biomasie gorczycy oraz wyraźnej poprawy stosunków K : Mg i K : Na, których wartość zbliżała się do optimum, a także Ca : Mg, jednak nie doprowadzając tej relacji do wartości optymalnej.

Przyczyną pogorszenia stosunków Ca : P, K : Ca i K : (Ca + Mg) jest duża zawartość Ca w biomasie roślin wynikająca ze względnie dużej zawartości Ca w osadzie dennym, mimo zastosowanego nawożenia mineralnego NPK oraz antagonizm między pierwiastkami. Przyczyną modyfikacji relacji między makroelementami mogą być zmiany odczynu podłoża w następstwie dodatku osadu dennego do gleby, zwłaszcza wynoszącego (3–20) % masy podłoża, które powodowały wzrost wartości pH proporcjonalny do udziału osadu. Największe dodatki osadu doprowadzały odczyn podłoże do zbliżonego do obojętnego.

Osad denny bagrowany ze Zbiornika Rożnowskiego może być użyty do poprawy właściwości gleb lekkich kwaśnych, może jednak powodować pogorszenie się stosunków masowych między wapniem a pozostałymi makroelementami, zwłaszcza P i K.

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

DOI: 10.2428/ecea.2012.19(04)041 ECOL CHEM ENG A. 2012;19(4-5):395–402

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TOTAL CHROMIUM AND NICKEL CONTENTS AND SOLUBLE FORMS OF THESE METALS IN COMPOSTS

OGÓLNA ZAWARTOŚĆ CHROMU I NIKLU ORAZ ROZPUSZCZALNYCH FORM TYCH METALI W KOMPOSTACH

Abstract: Composting is one of the methods of household sewage sludge management which ensures obtaining a product of high fertiliser quality, without the risk of soil contamination. Among preconditions is the appropriate chemical composition of the sewage sludge, especially with regard to the content of heavy metals, its stability as well as the proper choice of biodegradable wastes added to the sludge. The studies aimed at determining the impact of various organic substances added to sewage sludge on changes in the total content of chromium and nickel and water soluble forms of these metals in composts.

The experiment was carried out on the premises of an open compost plant using the method of compost piles which were made up of sewage sludge supplemented with industrial wastes from hemp or/and straw and wood chips, depending on the adopted experimental design. Composting until the end of the cooling phase lasted 93 days and the remaining 131 days were treated as the maturing phase. A tractor aerator was employed in the trial to spread, chop and aerate the composted material.

It was found that the strongest influence on the total content of chromium and nickel in composts was exerted only by the time of composting. In the case of soluble forms, time also exerted the strongest impact, although in the case of chromium compounds, additionally, the type of compost as well as the joint action of these two factors was also important.

Keywords: sewage sludge, organic wastes, composts, chromium, nickel

Introduction

Composting as a method for biological utilization of biodegradable wastes [1–3] has been known for ages and successfully used for utilizing the sewage sludge [4–8]. Data collected by Polish *Central Statistical Office* [9] revealed that 526.7 Mg of dry sludge was generated in Poland in 2010, including 20.7 % used in agriculture and 11.2 % stored in dumps. According to assumptions of National Plan for Wastes management [10], about 15 % of produced sludge are intended to be directed for composting in 2010 with perspectives of enhancing that proportion to 20 % in a future. Therefore, it is important to recognize in details all technological aspects as well as changes occurring

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during composting process. It also refers to transformations of heavy metals that are integral part of sewage sludge [11, 12]. Heavy metals are present in sewage sludge at varied contents [13], which is reflected in composts produced using the sludge [14]. However, not only metals quantities, but also their chemical bindings have become the subject of studies for many years. It is associated, among others, with the risk estimation after sludge and other wastes introduced into the soil. Therefore, research upon the solubility of heavy metals forms contained in sewage sludge, thus their potential availability for plants, is an important element of composts assessment.

The study aimed at evaluating the influence of different bioorganic additives to municipal sewage sludge on changes in total contents of chromium and nickel and their water-soluble forms in composts.

Material and methods

The research was carried out in an open composting plant in 2007 applying mainly sewage sludge mixed – according to study scheme (Table 1) – waste hemp, wooden chips and/or straw. The percentage of individual components – recalculated onto dry matter – is presented in Table 1.

Table 1

Share in composts

Waste	Compost		
	1	2	3
	Share [%]		
Sewage sludge	30.6	32.8	37.6
Hemp waste	69.4	60.4	47.6
Straw	—	6.8	—
Wooden chips	—	—	14.8
Total	100	100	100

Sewage sludge, like other waste materials used, was characterized by various chemical composition, which is illustrated in Table 2.

Table 2

Selected properties of sewage sludge and organic wastes

Component	Dry matter	C_{org}	N_{tot}	C : N	C_{tot}	Ni_{tot}
	$[g \cdot kg^{-1}$ d.m.]				$[mg \cdot kg^{-1}$ d.m.]	
Sewage sludge	11.71 ± 0.39	481.3 ± 4.26	56.74 ± 0.69	8.48	158.80 ± 1.35	21.21 ± 0.54
Straw	90.44 ± 1.96	415.7 ± 1.11	46.39 ± 0.10	123.26	1.11 ± 0.06	0.93 ± 0.11
Hemp waste	77.62 ± 0.95	416.0 ± 2.14	10.05 ± 0.35	41.39	2.97 ± 0.24	2.74 ± 0.13
Wooden chips	45.58 ± 1.12	463.0 ± 1.07	3.36 ± 0.11	137.80	2.01 ± 0.04	2.05 ± 0.09

Organic materials were stacked up in layers in each prism with the straw as a bottom layer not taken into account in the qualitative balance. Prepared components were put in a following sequence: straw – sludge – wastes, and then all these were shoveled using tractor aerator. The aerator shoveled, aerated, and crumbled material. The prism shoveling was made once a week during the first composting month, and then, depending on the temperature of composting matter. The process persisted 93 days, after which the prism was transferred onto its maturation place lasting another 131 days. In the course of the experiment, samples for analyses were collected but because of the quantities of data, the data presented in the paper include only information from the day of establishment of the trial (day 0), after 93 days (end of the cooling down period) and after the termination of maturing (131 days), *ie* the total of 224 days of the duration of the entire experiment.

The material for analyses in the amount of six samples was, every time, collected from the central area of the heap which, following their mixing and grinding, constituted a mean sample. All analyses were carried out in three replications.

Compost samples were subject to following determinations: dry matter – drier method at 105 ^{o}C, reaction – $pH_{(H_2O)}$ – conductometry, organic matter – combusting at 550 ^{o}C, organic carbon – redox method with potassium dichromate in acidic medium, total nitrogen – Kjeldahl's method. Chromium and nickel were determined by means of *atomic absorption spectrophotometry* (AAS). Prior to analyses, total chromium and nickel were prepared by combusting samples (dry matter) at 550 ^{o}C and dissolving achieved ash in hot 3 mol · dm^{-3} HCl solution for 3 hours under cover. Soluble forms of both analyzed elements were obtained from the water extracts of composts (compost : water 1:10, w/v), part of which was evaporated till dryness, the remains were combusted at 550 ^{o}C (30 minutes), and the ash was dissolved in hot 3 mol · dm^{-3} HCl solution [15].

The statistical assessment of the obtained results was performed on the basis of the multifactorial analysis of variance and the significance of differences between means was determined using Duncan test at the level of significance of $\alpha = 0.05$. Calculations were carried out with the assistance of the STAT program.

Results and discussion

During the process of composting, organic matter undergoes decomposition the consequence of which is, among others, increase of ash quantities. This, in turn, causes observed increases of many elements in the composted material [16]. However, the rate of these transformations differs and, in general, varies between individual elements. For instance, Amir et al [17] determined a significant correlation between ash content in the composts from sewage sludge and Ni and Cu quantities soluble in water. On the other hand, no such correlation was found for Zn and Pb. Correlations between the above-mentioned parameters represent only a few of those that can be observed in composts. They appear to be the outcome of, among others, the initial content of chemical elements from individual constituents as well as the strength of their complexing with individual, primarily organic, constituents of wastes.

Transformations of compost constituents were strongly influenced by the time of composting as well as by the composition of the composting mass [2]. When composting animal manure, above authors found the increase of majority of examined heavy metals contents, namely chromium and nickel. The demonstrated tendencies are, undoubtedly, associated with properties of the metal itself as well as with the bond stability with organic matter which, in turn, may exert impact on the dynamics of the release of individual metals during the composting process.

Taking into account data presented in the study, it is evident that the impact of experimental factors separately on the content of different forms of chromium and nickel varied.

The effect of the kind of compost, consequently, indirectly of their composition, on the total content of the two elements turned out to be non-significant ($p < 0.05$) (Table 3).

Table 3

Effect of the compost type, irrespective of the days of composting, on the content of chromium and nickel in composts [$mg \cdot kg^{-1}$ d.m.]

Compost	Chromium		Nickel	
	form			
	total	soluble forms	total	soluble forms
1	33.82	0.455^b	23.18	0.586
2	37.23	0.478^b	24.81	0.597
3	36.59	0.352^a	24.15	0.499

a, b – means marked with different letters in columns are significantly different at $p < 0.05$.

It was in contrast to results achieved by Yanez et al [18]. When composting the sewage sludge with various proportions of industrial waste of silver wattle, they found great initial differentiation of total chromium and nickel contents, the amounts of which increased along with the increase of the sludge share in the composting mixture. After composting complete (43 days), contents of both elements were lower in all composts than those determined at the experiment beginning day. In composts, this phenomenon is associated, most frequently, with the advancing degradation of organic matter in the process of mineralisation [19, 20].This, in general, is accompanied by the increase in the ash content [21]. It is evident from the data [22] that, depending on the composition of composted mixtures, the increase in heavy metal concentrations in mature composts constituted from 14 % to 85 % in comparison with the initial content.

Changes in element contents in composts due to their initial composition also refer to macrocomponents, both in a view of compost type and the process duration, which was confirmed by Czekala [8]. On the other hand, data presented in Table 4 indicate a significant impact of time, as an experimental factor, on changes in total contents of chromium (F = 144.30**) and nickel (F = 146.91**). Attention should also be drawn to similar tendencies of changes for chromium and nickel contained in the same uniform groups in composts despite differences in the level of content of each element. In both cases, by the end of the cooling down phase (the 93rd day of composting), the content of Cr increased on average by 38.6 % and that of Ni – by 52.5 %. Compost maturation contributed to the reduction in the content of both elements but to a different degree.

The content of Cr amounted, on average, to 23.17 mg · kg^{-1} and that of Ni – to 18.23 mg · kg^{-1} (Table 4). This means that this decline amounted to about 44.1 % for total nickel and to about 52.8 % for total Cr in relation to the quantity from the cooling down phase.

Table 4

Effect of composting time, irrespective of the type of compost, on the content of chromium and nickel in composts [mg · kg^{-1} d.m.]

Days of composting	Chromium		Nickel	
	total	soluble forms	total	soluble forms
0	35.40^{b}	0.620^{c}	21.40^{b}	1.106^{b}
93	49.08^{c}	0.378^{b}	32.63^{c}	0.225^{a}
224	23.17^{a}	0.286^{a}	17.95^{a}	0.351^{a}

a, b... – means marked with different letters in columns are significantly different at $p < 0.05$.

No significant ($p < 0.05$) synergistic effect of the two experimental factors was observed on the level of total Cr and Ni content as well as of their unambiguous directions of their quantitative changes (Table 5).

Table 5

Impact of the cooperation of experimental factors on the total content of chromium and nickel and their soluble forms in composts

Element	Composts								
	1			2			3		
	Days of composting								
	0	93	224	0	93	224	0	93	224
Total content [mg · kg^{-1} d.m.]									
Cr	32.56	46.24	22.65	37.96	50.54	23.20	35.68	50.44	23.65
Ni	19.87	31.44	17.76	22.66	33.58	18.20	21.66	32.87	17.90
Content of soluble forms [mg · kg^{-1} d.m.]									
Cr	0.519^{de}	0.430^{cd}	0.418^{cd}	0.746^{f}	0.394^{bc}	0.294^{b}	0.596^{e}	0.312^{bc}	0.146^{a}
Ni	1.131^{b}	0.266^{a}	0.362^{a}	1.172^{b}	0.246^{a}	0.372^{a}	1.016^{b}	0.163^{a}	0.320^{a}

a, b... – means marked with different letters in rows are significantly different at $p < 0.05$.

This was probably caused by a strong influence of the time factor at the simultaneous negligible impact of compost composition. This possibility is indicated, among others, by investigations carried out by Jakubus [14] who demonstrated that chips and sawdust alone affected only slightly the total quantity of heavy metals in composts and significant differences in the content of heavy metals were only observed after the introduction into the compost mixtures of different quantities of sewage sludge. It seems that, when analyse the above problem, properties of the element itself should also be taken into account as indirectly indicated by investigations carried out by Ko et al [23] who reported increased content of the examined metals in the course of the composting process but with the weakest dynamics in the case of chromium and nickel. However, it should be emphasised that such changes refer not only to micro- but also macroelements [8].

In the case of total contents of metals (Table 5), despite the above-mentioned lack of cooperation of the experimental factors, two phases of changes were observed. The first of them was connected with the increase in the Cr and Ni content during the first three months of the trial which, on average, constituted from 33.0 % to 42.0 % in relation to the initial content of chromium and from 48.2 % to 58.2 % in the case of nickel. The second phase was associated with quantitative losses of both elements both in relation to their content on the day of establishment of the compost heaps as well as during the phase of cooling down. The above changes could have been caused, primarily, by the high dynamics of organic matter degradation during the initial period of the composting process resulting in release of metals. On the other hand, their losses observed in mature composts were caused, to a considerable extent, by leaching during the autumn-winter period. Simultaneously, the observed greater dynamics in quantities of Ni could have resulted from easier release of the metal from organic bonds in relation to chromium, the element which forms relatively strong bonds with organic compounds [24].

Chromium and nickel are characterised by a relatively small albeit varying solubility. This is corroborated by data presented in Tables 3–5. It is evident from them that, out of the two metals, quantities of the easily available forms declined with the time of composting, but only with respect to chromium. The determined correlations resulted, to a certain degree, from the character of Cr and Ni bonds in sewage sludge. It was demonstrated [25] that, generally speaking, 80 albeit 90 % of chromium in sewage sludge occurred in poorly soluble or non-soluble bonds, whereas almost 20 % of Ni was found in bonds of residual fraction.

However, assessment of metal solubility in compost may differ depending on applied extracting agent. Krzywy et al [26], when used 0.5 mol $\cdot$ dm^{-3} HCl solution to evaluate some metals solubility properties, did not find any influence of the compost type and composting duration on qualitative changes of examined elements. However, large ionic strength of the extracting agent and its controversial usefulness for composts, should be also taken into account.

Regardless of these above remarks, own study revealed that chromium solubility decreased along with the composting duration on average from 1.75 % at the experiment beginning day to 0.80 % in matured compost. In the case of nickel, these changes were characterized by varied tendency in time from 5.17 % at the beginning to 1.92 % at the end of experiment.

Possibility to loose metals during composting process, namely under conditions of open composting plants, is another issue. During composting, when temperature in a prism arises, chemically bound water is released along with components of composted materials, which seems to be one of the most important sources of observed metal losses. The range of these losses depends on the chemical nature of individual elements bindings, namely on a solid fraction of composts.

Conclusions

1. Total contents of chromium and nickel in composts containing sewage sludge was significantly determined only by composting duration.
2. Along with time, total amounts of chromium and nickel in composts increased till the end of cooling phase with subsequent decrease at the final maturity stage.
3. No significant influence of the compost type and composting duration on total chromium and nickel content as well as water-soluble nickel forms in compost, was recorded.
4. The type of organic waste used for composting sewage sludge has differently influenced metals solubility, which was in turn substantially modified by the duration in composting.
5. Among all organic wastes, the addition of wood loggings decreased mostly the solubility, particularly of chromium.

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OGÓLNA ZAWARTOŚĆ CHROMU I NIKLU ORAZ ROZPUSZCZALNYCH FORM TYCH METALI W KOMPOSTACH

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Abstrakt: Kompostowanie jest jedną z metod utylizacji komunalnych osadów ściekowych, zapewniającą otrzymanie produktu o wysokiej wartości nawozowej, bez ryzyka skażenia gleby. Jednym z warunków spełniającym takie wymogi jest prawidłowy skład chemiczny samych osadów, szczególnie pod kątem zawartości metali ciężkich, jego stabilizacja oraz właściwy dobór odpadów biodegradowalnych dodawanych do osadów. Przeprowadzone badania miały na celu określenie wpływu różnych dodatków organicznych do osadów na zmiany ogólnych zawartości chromu i niklu oraz ich wodnorozpuszczalnych form w kompostach.

Doświadczenie przeprowadzono na terenie kompostowani otwartej metodą pryzm, które utworzono z komunalnych osadów ściekowych z dodatkiem przemysłowych odpadów z konopi lub/i słomy oraz zrębków drzewnych, w zależności od schematu badań. Kompostowanie do końca fazy schłodzenia trwało 93 dni i dalsze 131 dni w fazie dojrzewania. W pracy wykorzystano aerator ciągnikowy, który przerzucał, rozdrabniał i napowietrzał kompostowany materiał.

Stwierdzono, że czynnikiem w największym stopniu wpływającym istotnie na ogólną zawartość chromu i niklu w kompostach był tylko czas kompostowania. W przypadku rozpuszczalnych form tych metali także czas działał najsilniej, a w odniesieniu do związków chromu dodatkowo rodzaj kompostu i współdziałanie obu czynników.

Słowa kluczowe: osady ściekowe, odpady organiczne, komposty, zawartość chromu, zawartość niklu

DOI: 10.2428/ecea.2012.19(04)042 ECOL CHEM ENG A. 2012;19(4-5):403-410

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EVALUATION OF THE IMPACT OF THE COPPERWORK “GLOGOW” ON THE TOTAL CONTENT OF MANGANESE AND ITS MOBILE FORMS IN THE VICINITY OF ARABLE SOILS

OCENA ODDZIAŁYWANIA HUTY MIEDZI „GŁOGÓW” NA ZAWARTOŚĆ CAŁKOWITĄ MANGANU ORAZ JEGO FORM MOBILNYCH W OKOLICZNYCH GLEBACH UPRAWNYCH

Abstract: The occurrence of manganese in soils depends *eg* on its content in the parent rock as well as on the soil-formation process determining its profile distribution. Moreover clay soils are richer in this metal than sandy soils.The properties and transformations of manganese compounds are defined by redox conditions as well as the reaction and the content of organic substance and calcium carbonate.

The aim of the present research was to determine the total contents of manganese and its mobile forms in the profiles of Luvisols in the vicinity of the Copperworks “Glogow”.

The research material was made up of the profiles of arable Luvisols located at different distances from the Copperworks “Glogow”. There were made four soil test pits located at varied distances from the emitter: P1 – 6.8 km (southwards), P2 – 6.6 km (south-eastwards), P3 – 5.7 km (eastwards) and P4 – 6.5 km (southwards). In the soil samples from each genetic horizon the following soil analyses were made: texture using Cassagrande method with the modification by Pruszynski, pH in H_2O and in the KCl solution (1 mol/dm^3) using potentiometric method, C_{org} using Tiurin method, content of $CaCO_3$ by Scheibler volume method [3]. The total content of manganese was defined with the AAS method following the mineralization in the mixture of HF and $HClO_4$ acids and the content of mobile manganese forms, according to the modified sequence analysis by Miller et al (1986). The soils investigated were classified as the subtype of Haplic Luvisols showing the reaction ranging from slightly acid to alkaline and the content of C_{org} in horizons Ap from 6.7 g $\cdot$ kg^{-1} to 31.2 g $\cdot$ kg^{-1}. The total content of manganese ranged from 102.40 g $\cdot$ kg^{-1} to 332.80 mg $\cdot$ kg^{-1}. The Mn-richest horizons were the humus horizons, while Mn lowest contents were observed in the horizons of the parent rock in all the profiles investigated. In the sequential analysis the most important share (about 41 %) in the total content of manganese was reported for fraction IV (connected with organic matter) and fraction VI – connected with crystalline iron oxides (24 %) and fraction III – with free manganese oxides (15 %). The share of fractions 1, 2 and 5 was below 5 % of the total content of the metal. A considerable content of Mn fractions connected with organic matter and iron and manganese oxides points to its temporary immobilization, which

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is connected with the changes in the redox potential. The total contents do not exceed the geochemical background level, which allows for considering the soils of that region to be unpolluted with manganese.

Keywords: soil, total manganese, mobile forms, sequential analysis

Introduction

Manganese is one of the metals classified as representing the group posing a high potential threat for the environment [1, 2]. It occurs in the soil mostly in a form of free oxides or silicates from which, as a result of the process of weathering, Mn^{2+} ions get released, entering the soil solution. The content of manganese in soil undergoes many fluctuations, and the variation in its content, next to manganese richness of the soils parent rocks, is affected by the physicochemical conditions of the environment. Besides the redox conditions, also the reaction and the content of organic substance and calcium carbonate determine the transformations of manganese compounds in soil. The anthropogenic factors resulting in the increase in the content of heavy metals in the agricultural environment include dust emissions from the copper smelter and refinery of non-ferrous metals, which is especially dangerous in soils due to their adsorption in mineral and organic colloids. In Poland the main copper producer is KGHM POLSKA MIEDZ S.A. It covers the Copperworks “Glogow” I and II as well as the Copperworks “LEGNICA”. They are located at a small distance from the areas under the agricultural use, which makes their contamination with the emissions from the Copper Smelter and Refinery more likely.

The aim of the present research was to evaluate the impact of the Copperworks “Glogow” on the total content of manganese and its mobile forms in the arable profiles of Luvisols.

Material and methods

The research of the soil cover involved the area located in the vicinity of the Copperworks “Glogow”. There were made four soil test pits located at varied distances from the emitter: P1 – 6.8 km (southwards), P2 – 6.6 km (south-eastwards), P3 – 5.7 km (eastwards) and P4 – 6.5 km (southwards). During the field research, drawing on the morphological features, in selected soil profiles there were separated genetic horizons from which soil was sampled and the following laboratory analyses were made: the grain size composition with the Cassagrande method modified by Proszynski, pH with the potentiometric method in H_2O and in the KCl solution at the concentration of $1 \text{ mol} \cdot \text{dm}^{-3}$, C_{org} applying the Tiurin method, the content of $CaCO_3$ with the volumetric method by Scheibler [3]. The total contents of manganese were determined following the soil mineralization in the mixture of HF and $HClO_4$ acids, using Crock and Severson’s procedure [4]. The extraction of mobile forms of manganese was made drawing on the modified [5] sequential analysis according to Miller et al [6], which allowed the separation of metal fractions, following: FI – exchangeable and soluble in water fraction, FII – forms soluble in acids, F3 – forms occluded on manganese oxides, FIV – forms associated with organic matter, FV – lead bound to amorphous iron oxides, FVI – forms associated with crystalline iron oxides, FVII – residual forms. There was also made the analysis of certified material Till-3 and SV-M. The measurements of the contents of total and mobile Mn forms were performed with the *Atomic Absorption Spectrometry* (AAS) applying the PU 9100X spectrometer. The analysis mas made in three repetitions. The statistical evaluation of the results was made with the use of Statistica 10.0 software.

Results and discussion

The arable soil profiles selected for the present research have been classified to represent a good wheat complex. While applying agricultural categories [7], they belong to medium heavy soils (P1 and P2) and heavy soils (P3 and P4). According to the PTG 2008 soil classification, they have been considered to represent Haplic Luvisols produced from silts [8] with the sequences of genetic horizons (Ap, Eet, Bt, C) typical for those soils.

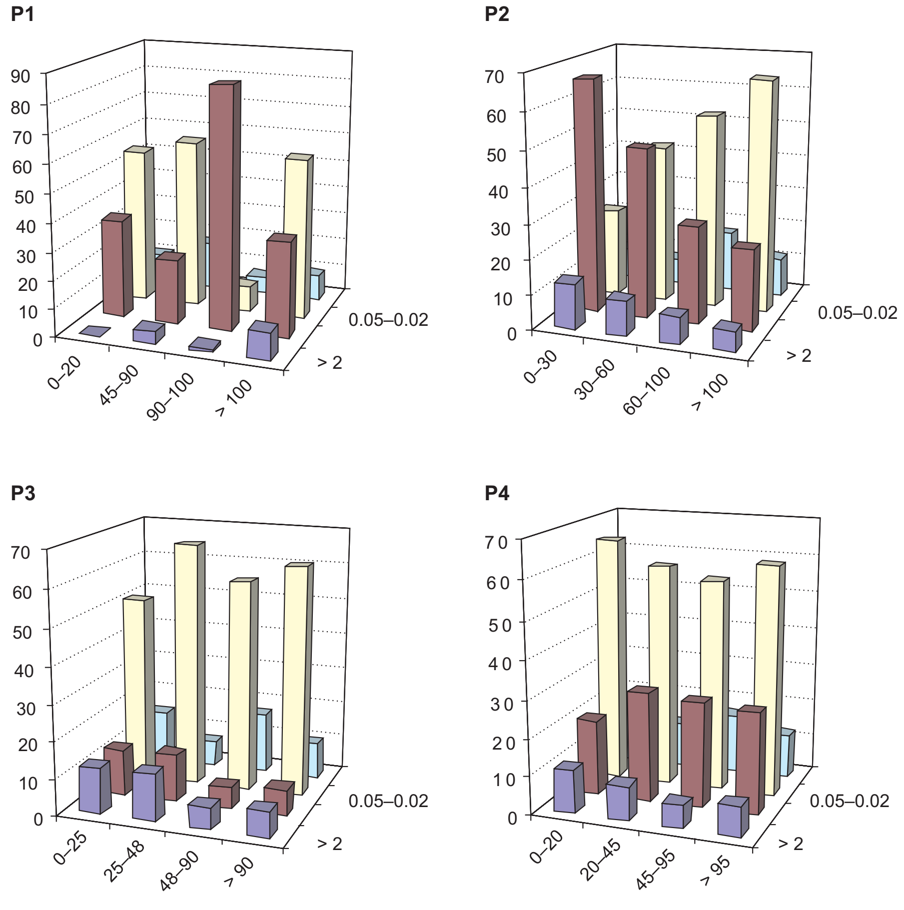

Fig. 1–4. Percentage of fraction with diameter [mm]

The feature characteristic for the grain size composition of the soils investigated was a low content of skeleton fractions (5; 15) %, which facilitates their classification as poor-skeleton formations [7].

In the parent rocks of the soils analysed there occurs the grain size composition of silt loams (Fig. 1–4), and in the enrichment horizons – silt loams. In all the profiles there was found a clear enrichment of illuvial horizons with all the clay fraction in which the sub-fraction of fine clay (∅ 0.0002 mm) prevailed. In the humus and eluvial horizons of the profiles investigated (except for profile P2), the grain size composition corresponds to silt loams (Fig. 1–4). The grain size composition results from the aerometric analysis demonstrated that the dominant grain size composition group in the profiles analysed was silt loam [7]. The content of the clay fraction, next to the content of C_{org} and the reaction, is the factor which has a considerable effect on the availability of heavy metals [9]. The soils showed the content of organic carbon, typical for the soils of that region, which in the humus horizons ranged from 7.0 $g \cdot kg^{-1}$ to 18.1 $g \cdot kg^{-1}$ (Table 1). The organic substance in the soil and that introduced with fertilisers result in limiting the availability of heavy metals and thus their toxicity decreases [10]. The reaction of the soils investigated was neutral and close to alkaline pH_{H_2O} (7.33; 8.55) and pH_{KCl} (5.81; 7.75). The more acid the soil, the more soluble and the more available the manganese compounds. Besides, the higher pH values, the higher concentration of Mn^{2+} ions available to plants. Clearly lower pH values were recorded in the illuvial horizons (Table 1). The alkaline reaction of the soils investigated could have been affected by intensive liming of arable soils around the Copperworks, which was to limit the uptake of heavy metals from the sorption complex of soils and manganese leaching to deeper horizons [9]. What is noteworthy is the presence of calcium carbonate (0.43; 11.6) % in most samples, which, however, does not always determine a high pH value (Table 1). The total contents of manganese in the profiles investigated assumed the values in the range 59.2 $mg \cdot kg^{-1}$ to 332.8 $mg \cdot kg^{-1}$ (Table 2). The occurrence of manganese in soils depends on the anthropogenic factors and on its content in the parent rock as well as on the soil-formation process determining its profile distribution [11, 12]. The manganese content is usually higher in the soils rich in the clay fraction [13]. The soil richness in the fraction of colloidal clay as well as the humus content affect the availability of heavy metals to plants [9]. Manganese deficits can be due to its immobilisation in organic soils and containing carbonates. In all the soils investigated clearly higher total manganese contents were in the humus horizons, while the lowest contents were reported in the horizons of the parent rock (Table 2). The high content of C_{org} was accompanied by the highest total manganese content (profile P1). There was no correlation between the total content of manganese and the content of fraction with ∅ < 0.002 mm, differently to other authors [13]. The pollution of soils with manganese is connected with its form and not with the amount. The knowledge of the total contents of heavy metals in soils does not provide the picture of their real availability to plants and the possibility of entering into the biological circle [15] which however, is possible with the sequential analysis [16]. Application of sequential extraction allows the evaluation of metals behavior in soil environment and the possibility of their migration to biochemical circulation [17]. This may be the result of the increased accumulation of heavy metals in the agricultural areas located within the range of metalliferous dusts emission [9].

In the sequential analysis applied [5, 6] there were separated seven manganese fractions: FI – exchangeable and soluble in water fraction, FII – forms soluble in acids, F3 – forms occluded on manganese oxides, FIV – forms associated with organic matter, FV – lead bound to amorphous iron oxides, FVI – forms associated with crystalline iron oxides, FVII – residual forms (Table 2).

Table 1

Physico-chemical properties of the soils

Profile Horizon	Depth [cm]	pH		$CaCO_3$ [%]	C_{org} [$g \cdot kg^{-1}$]
		H_2O	KCl		
P1					
Ap	0–20	7.33	6.07	< 1	18.1
Eet	20–45	7.54	5.91	< 1	3.2
Bt	45–90	7.95	5.81	< 1	n.o.
C	90–100	8.16	6.62	< 1	n.o.
C1	> 100	8.14	6.58	< 1	n.o.
P2					
Ap	0–30	7.53	6.89	< 1	7.2
Eet	30–60	8.20	7.50	< 1	3.9
Bt	60–100	7.82	6.46	11.6	n.o.
C	> 100	8.48	7.65	< 1	n.o.
P3					
Ap	0–25	8.19	7.49	1.93	7.0
Eet	25–48	8.55	7.72	< 1	1.2
Bt	48–90	8.13	7.30	6.72	n.o.
C	> 90	8.38	7.75	8.58	n.o.
P4					
Ap	0–20	7.55	7.22	< 1	18.4
Eet	20–45	7.53	7.05	< 1	4.9
Bt	45–95	7.67	6.98	3.46	n.o.
C	> 95	8.01	7.30	5.82	n.o.

The contents of manganese forms soluble in water (fraction I) were below the detection threshold, which could have been due to a high pH of the soils. Growing acidification strengthen the airing of minerals processes and the accumulation of their products in soil profile [18, 19].The exchangeable fraction (F II) accounted for 0.1–4 % of the total Mn content only, and its content in the profiles ranged from 0.8 mg $\cdot$ kg^{-1} to 14.0 mg $\cdot$ kg^{-1}.

A low content of the most mobile forms (FI and FII) points to a low bioavailability and toxicity of manganese in the soils. The presence of calcium carbonate is a factor which limits the availability of manganese and its leaching into deeper soil layers. The fraction occluded (coprecipitated) on Mn oxides (FIII) was most abundant in the humus horizons (Table 2). Similarly, the humus horizons also demonstrated the highest content of fractions VI and VII; the forms connected with crystalline iron oxides and the residual forms. The fraction dominant in the profiles investigated was the one connected with organic substance (FIV) and its contents ranged from 30.0 mg · kg^{-1} to 130.0 mg · kg^{-1}. Manganese connected with organic substance can be temporarily immobilized. In the polluted soils there is observed a considerable share of the fractions connected with organic substance [16]. A considerable content of the least mobile Mn forms (FVI and FVII) points to a clear tendency to Mn occluding with iron oxides of soil minerals [17]. Determining the manganese mobility facilitated the evaluation of its possibility to enter the biogeochemical circle [20].

Table 2

The total content of manganese and metal fractions in soils

Profile Horizon	Total Mn [mg · kg^{-1}]	F I	F II	F III	F IV	F V	F VI	F VII*
		[mg · kg^{-1}]						
P1								
Ap	44.64	b.d.	14.0	26.8	130.0	17.6	100.4	44.0
Eet	31.36	b.d.	4.0	9.2	57.6	18.4	98.0	26.8
Bt	30.16	b.d.	2.4	5.2	30.0	14.0	73.2	27.2
C	27.16	b.d.	1.6	3.6	52.0	9.2	34.0	15.6
C1	27.36	b.d.	1.6	1.6	36.0	0.8	7.2	12.0
P2								
Ap	31.44	b.d.	2.4	26.8	90.0	8.4	60.0	30.0
Eet	23.84	b.d.	2.0	14.4	104.4	10.8	50.0	22.0
Bt	24.48	b.d.	2.4	9.2	34.0	7.6	25.2	24.0
C	21.96	b.d.	0.8	76.6	69.2	2.8	20.0	15.6
P3								
Ap	34.68	b.d.	3.2	60.8	144.0	9.6	45.2	32.0
Eet	17.56	b.d.	0.8	23.2	109.2	8.4	16.8	17.2
Bt	22.44	b.d.	1.6	68.8	74.0	2.0	25.2	27.6
C	17.40	0.24	1.2	76.0	49.2	0.8	16.8	20.4
P4								
Ap	45.36	b.d.	4.4	35.2	84.0	9.2	51.2	24.0
Eet	34.80	b.d.	4.0	26.0	76.0	8.4	46.0	20.0
Bt	32.44	b.d.	2.8	9.6	82.0	16.0	56.8	18.8
C	28.72	b.d.	1.2	6.0	48.0	12.4	42.0	20.8

* FI – exchangeable and soluble in water fraction, FII – forms soluble in acids, F3 – forms occluded on manganese oxides, FIV – forms associated with organic matter, FV – lead bound to amorphous iron oxides, FVI – forms associated with crystalline iron oxides, FVII – residual forms, b.d. – below detection limit.

Conclusions

1. In the soil profiles in the vicinity of the Copperworks “Glogow” the total manganese contents fell within the range of (59.2; 332.8) mg · kg^{-1}. A clear enrichment in that element was found in the humus horizons, however, the contents did not exceed the geochemical background level.

2. In the sequence analysis the most considerable share in the total manganese content was reported for fraction IV (forms associated with organic matter), which accounted for (20; 62) % of the total content, and fraction VI (forms associated with crystalline iron oxides), – for (10; 48) % of the total content.

3. In the soils a low share of the most mobile fractions (FI and FII) can suggest a low manganese mobility and demonstrates its low bioavailability and toxicity.

4. The proximity of Copperworks “Glogow” did not affect on the increase of manganese concentration in nearby arable soils, which does not eliminate the investigated soils from their agricultural use.

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OCENA ODDZIAŁYWANIA HUTY MIEDZI „GŁOGÓW" NA ZAWARTOŚĆ CAŁKOWITĄ MANGANU ORAZ JEGO FORM MOBILNYCH W OKOLICZNYCH GLEBACH UPRAWNYCH

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Abstrakt: Występowanie manganu w glebach zależy m.in. od jego zawartości w skale macierzystej, jak również od procesu glebotwórczego decydującego o jego profilowym rozmieszczeniu. Obecne w skale macierzystej metale ciężkie są na ogół mało ruchliwe i uwalniane są dopiero w wyniku procesów wietrzenia. O właściwościach i przeobrażeniach związków manganu decydują poza warunkami redoks, także odczyn oraz zawartość substancji organicznej i węglanu wapnia.

Celem przedstawionych badań było określenie całkowitych zawartości manganu oraz jego form mobilnych w profilach gleb płowych z sąsiedztwa Huty Miedzi Głogów.

Materiał badawczy stanowiły profile uprawnych gleb płowych położonych w różnej odległości od Huty Miedzi „Głogów". Wykonano cztery odkrywki glebowe zlokalizowane w różnej odległości od emitora: P1 – 6,8 km (w kierunku południowym), P2 – 6,6 km (w kierunku południowo-wschodnim), P3 – 5,7 km (w kierunku wschodnim) i P4 – 6,5 km (w kierunku południowym). W wybranych profilach glebowych wyodrębniono poziomy genetyczne, z których pobrano próbki glebowe i wykonano następujące analizy laboratoryjne: uziarnienie metodą Casagrande'a w modyfikacji Prószyńskiego, pH metodą potencjometryczną w H_2O i w roztworze KCl o stężeniu 1 mol $\cdot$ dm^{-3}, C_{org} metodą Tiurina, zawartość $CaCO_3$ metodą objętościową Scheiblera [3].

Całkowitą zawartość manganu oznaczono metodą AAS po mineralizacji w mieszaninie kwasów HF i $HClO_4$, a zawartość form mobilnych manganu, wg zmodyfikowanej analizy sekwencyjnej Millera i in. (1986). Badane gleby zaliczono do podtypu gleb płowych typowych o odczynie w zakresie od lekko kwaśnego do zasadowego i zawartości C_{org} w poziomach Ap w przedziale (6,7; 31,2) g $\cdot$ kg^{-1}. Całkowita zawartość manganu wynosiła (102,40; 332,80) mg $\cdot$ kg^{-1}. Najzasobniejsze w mangan były poziomy próchniczne, natomiast najmniejsze jego zawartości stwierdzono w poziomach skały macierzystej we wszystkich badanych profilach. W analizie sekwencyjnej najbardziej znaczący udział w zawartości całkowitej manganu miała frakcja IV – związana z materią organiczną (około 41 %) oraz VI – związana z krystalicznymi tlenkami żelaza (24 %) i III – związana z wolnymi tlenkami manganu (15 %). Udział frakcji 1, 2 i 5 był poniżej 5 % zawartości całkowitej badanego metalu. Znaczna zawartość frakcji manganu związanych z materią organiczną oraz tlenkami żelaza i manganu wskazuje na jego czasową immobilizację, co związane jest ze zmianami potencjału oksydacyjno-redukcyjnego. Zawartości całkowite nie przekraczają poziomu tła geochemicznego, co pozwala uznać gleby tego regionu za niezanieczyszczone manganem.

Słowa kluczowe: gleba, mangan całkowity, formy mobilne, analiza sekwencyjna

DOI: 10.2428/ecea.2012.19(04)043 ECOL CHEM ENG A. 2012;19(4-5):411-420

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ACCUMULATION OF HEAVY METALS BY *Silene vulgaris* OCCURRING ON SERPENTINE WASTE DUMP IN GROCHOW (LOWER SILESIA)

AKUMULACJA METALI CIĘŻKICH PRZEZ *Silene vulgaris* WYSTĘPUJĄCEJ NA HAŁDZIE ODPADÓW SERPENTYNITOWYCH W GROCHOWIE (DOLNY ŚLĄSK)

Abstract: The investigation involved serpentine waste dump in Grochow (Lower Silesia).Botanical composition of analyzed serpentine dumping ground was poor since in the areas subjected to examination there were designated only 30 vascular plant species classified mainly to three botanical families – Poaceae, Fabaceae and Asteraceae. Dominant species on dumping ground in Grochow was the only recognized species representing Caryophyllaceae – *Silene vulgaris.* Analysis of soils material proved that total contents of nickel, chromium, manganese and cobalt were higher than average quantities of these metals in soil environment. Mobile forms, available for plants, provided, in most cases, for only a small per cent of their total forms. In plant material originating from serpentine dumping ground their were recorded high concentrations of Ni, Cr and Co in comparison with their natural amounts. Concentrations of all the examined metals were higher in underground parts of *Silene vulgaris* than in aboveground parts.

Keywords: heavy metals, serpentine, spoil heaps, *Silene vulgaris*

Introduction

In Poland, the areas of surface soils featuring naturally high content of heavy metals are limited to a few calamine, ore-bearing areas and rare, specific for Lower Silesia, soils formed from serpentine rocks [1]. Serpentine rocks are to be found on the territory of Poland, covering the area of about 80 km^2 and they form several elevated mountain massifs in the foot of the Sudeten [2]. Polish serpentine soils occupy relatively small areas and therefore, they are not of economic value [3]. Lower Silesian serpentine rocks have been exploited for a long time as a basis of nickel and chromium mining. The

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evidence for the latter ones are old quarries, headings and mineral waste dumps with scarce vegetation growing there.

Relatively poor occurrence of plant species probably results from specific, extremely hard, unfavorable conditions typical for those places [4]. Detrital serpentine minerals characterize a number of disadvantageous properties. Low moisture, high (basic) pH, low content of nitrogen, phosphorus and calcium, high, potentially harmful concentration of manganese, nickel and cobalt provide for the disorders in plant growth and development [5, 6].

Toxic effect of heavy metals, deficit of macroelements and water in the ground, intensive insolation (especially in the case of mineral waste dumps) can favor the occurrence of plants specific for these conditions [2].

The aim of the work was determination of botanical composition of waste dump vegetation (exclusively vascular plants), as well as the degree of heavy metals accumulation in soil and plant material collected from serpentine waste dump in Grochow.

Material and methods

The area subjected to investigation is located about 70 km to the south from Wroclaw, and to the south-west direction from Zabkowice Slaskie within the territory of Bardo community.

Serpentine waste dump in Grochow was formed in connection with magnesite exploitation from mineral deposit within the range of Grochow Massif.

Serpentines building this massif were created as a result of alteration of ultrabasic and basic rocks in deep facies of contact metamorphism [7].

Outer serpentine dumping ground in Grochow, subjected to the examination, covers the area of about 36 hectares and is situated in the vicinity of magnesite exploitation range, map No. 1. The material for chemical analysis were soil samples (mainly detrial minerals) and plant samples from serpentine dumping ground in Grochow. In order to compare examination data, on large territory there were distinguished four areas, diversified both as to their succession and surface constitution. The material of dumping ground, collected from surface layer from the depth of 0–15 cm, was transported to the analytical laboratory after its previous preservation. The samples underwent the assay of reaction (pH) according to potentiometric method in 1 mol KCl solution. Total content of selected heavy metals (Ni, Cr, Co, Mn, Zn, Pb and Cu) was determined due to spectrometric analysis technique, after previous samples mineralization in 70 % (per)chloric(VII) acid. Soluble forms of selected metals, after extraction in 1 mol HCl dm^{-3}, were assayed by AAS method.

Plant material included above – and underground parts of *Silene vulgaris,* collected from four previously distinguished areas and preserved for further chemical analyses.

Plant material, cleaned, dried and ground, underwent dry mineralization at the temperature of 450 ^{o}C, and in the filtrates obtained there were assayed the following chemical elements Cr, Co, Mn, Zn, Pb and Cu according to AAS technique with the use of Spectra AA 220 Fast Sequential device. Inflated catchfly *Silene vulgaris* (Moench)

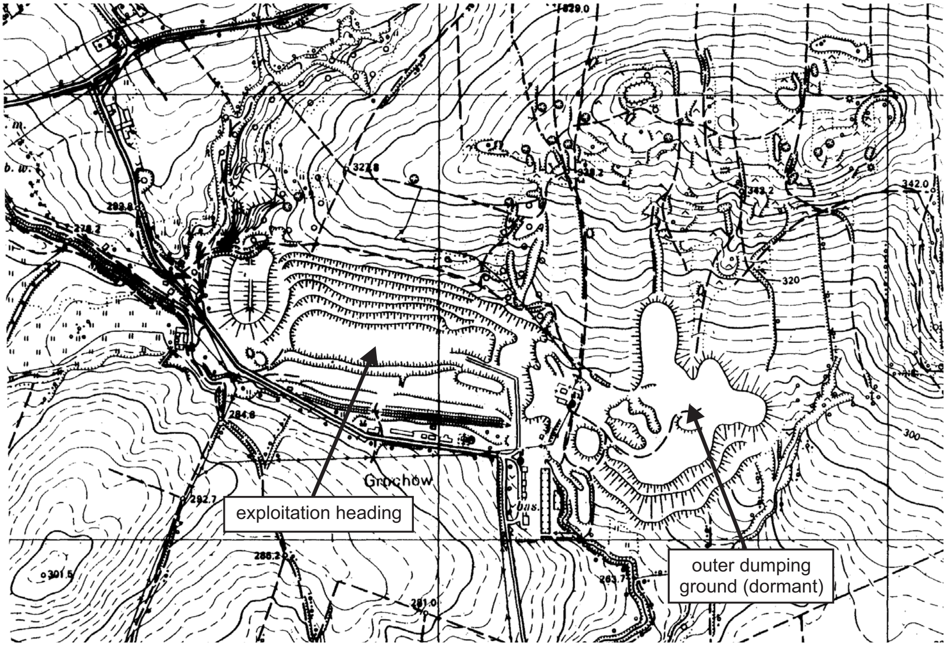

Fig. 1. Location of serpentine waste dump in Grochow (owned by Magnesite Plant "Grochow"' S.A. in Grochow)

Garcke is a perennial plant belonging to Caryophyllaceae family [8]. It commonly occurs in native territories of Europe, north Africa and Asia. This species has also spread in the areas of both Americas. In Poland *Silene* species can be fund on meadows, fields and forests [9], as well as on ruderal habitat sand the ones enriched with heavy metals, *eg* serpentine [10] or calamine waste dumps [11] as well as post-mining dumping grounds [12, 13].

Results and discussion

Botanical composition of serpentine waste dump

In the area of the examined serpentine waste ground in Grochow there were designated 30 species of vascular plants from 16 botanical families (Table 1). The presence of majority of these species on serpentine waste dump results from natural primary succession, while the remaining ones represent numerous seedlings of trees with some part of them planted within the frames of initial stage of waste dumps reclamation destined as afforested areas. Most commonly occurring botanical families on a waste dump were Poaceae and Fabaceae, as well as Asteraceae. The remaining families had their single representatives, yet very often dominating on a dumping ground, *eg Silene vulgaris* from Caryophyllaceae.

Table 1

Botanical composition of serpentine waste dump in Grochow

No.	Species	Family	Examined stand			
			1	2	3	4
1	*Achillea millefolium* L.	Asteraceae	+	–	–	–
2	*Anthylis vulneraria* L.	Fabaceae	+	–	+	–
3	*Apera spica-venti* (L.) P.B.	Poaceae	+	+	+	+
4	*Betula pendula* Roth seedlings	Betulaceae	–	+	+	+
5	*Bromus erectus* Huds.	Poaceae	+	+	+	+
6	*Calamagrostis epigeios* (L.) Roth	Poaceae	+	+	+	+
7	*Campanula rotundifolia* L.	Campanulaceae	+	+	–	–
8	*Carlina vulgaris* L.	Asteraceae	–	–	+	+
9	*Centaurea stoebe* L.	Asteraceae	+	+	+	–
10	*Cirsium arvense* (L.) Scop.	Asteraceae	–	+	–	–
11	*Koeleria macrantha* (Ledeb.) Schultes	Poaceae	+	+	+	+
12	*Daucus carota* L.	Apiacae	+	+	+	+
13	*Echium vulgare* L.	Boraginaceae	+	–	–	–
14	*Euphrasia rostcoviana* Hayne	Scrophulariaceae	–	+	–	–
15	*Festuca ovina* L.	Poaceae	+	+	+	+
16	*Galium verum* L.	Rubiaceae	+	+	–	–
17	*Genista tinctoria* L.	Fabaceae	+	–	–	–
18	*Hypericum perforatum* L.	Hypericacea	–	+	+	–
19	*Lathyrus sylvestris* L.	Fabaceae	–	+	+	–
20	*Leontodon hispidus* L.	Asteraceae	+	–	–	–
21	*Lotus corniculatus* L.	Fabaceae	+	+	+	+
22	*Melilotus alba* Medik.	Fabaceae	–	–	+	–
23	*Phleum pratense* L.	Poaceae	+	+	+	+
24	*Pinus silvestris* L. seedlings	Pinaceae	–	+	+	+
25	*Plantago media* L.	Plantaginaceae	+	–	–	–
26	*Potentilla recta* L.	Rosaceae	+	–	–	+
27	*Scabiosa ochroleuca* L.	Dipsacaceae	+	–	+	+
28	*Silene vulgaris* (Moench) Garcke	Caryophyllaceae	+	+	+	+
29	*Thymus pulegioides* L.	Labiatae	+	–	+	–
30	*Trifolium dubium* Sibth.	Fabaceae	–	+	–	–

On post-mining and post-industrial waste dumps spontanieous succession of plants requires a long time to take place [14]. Outer dumping of serpentine wastes in Grochow was made dormant only several years ago, which can explain its poor botanical composition. Relatively small number of plant species on serpentine dumping grounds and headings are confirmed by investigation conducted in this type of objects in Lower Silesia [10, 15].

Environmental conditions of waste dumps, effected by unfavorable properties of the ground and by exposure to intensive insolation and winds, find their reflexion not only in poor but also specific flora. Numerously occurring species of Poaceae, Fabaceae and Asteraceae families seem to be significant of anthropogenic serpentine habitats of Lower Silesia [10, 15]. The species designated as the waste dump in Grochowa are repeateably found on these types of objects in Naslawice, Wirki or Szklary.The species like *Silene vulgaris*, *Calamagrostis epigejos* or *Festuca ovina* are also enumerated regarding the composition of Polish natural serpentine plants communities [10, 15, 16].

Among designated in the whole examined area 30 species of vascular plants the highest number of them was fund on the stand No. 1–21 species, stand. No. 2 and 3 were the site of occurrence of 19 plant species and the lowest number belonged to stand No. 4–14 species. There were recorded 9 species common for all the areas, namely: *Apera spica-venti*, *Bromus erectus*, *Calamagrostis epigejos*, *Daucus carota*, *Festuca ovina*, *Koeleria macrantha Lotus corniculatus*, *Phleum pratense* and *Silene vulgaris*. On some stands there were also recognized plant species which did not grow on the remaining stands. Here can be distinguished the stand No. 1 covered by thick vegetation, located in some distance from serpentine waste dumps.

The content of selected heavy metals in soils

In the analyzed soil material originating from serpentine dumping ground the highest total concentrations of heavy metals belonged to nickel, chromium and manganese – Table 2.

Table 2

Soil reaction and the content of total forms of selected heavy metals in soil collected from serpentine waste dump in Grochow

Stand	Sample number	pH [1 mol KCl · $\mathrm{dm^{-3}}$]	Total forms content [mg · $\mathrm{kg^{-1}}$ of soil]						
			Ni	Cr	Mn	Co	Cu	Pb	Zn
1	1	7.9	3182	1033	1188	86.3	9.68	25.0	75
	2	7.8	2301	1088	813	64.0	8.45	28.5	53
	3	7.4	2052	984	915	64.5	13.93	36.3	73
2	4	8.7	1854	1155	1025	67.3	34.05	24.0	45
	5	8.7	1833	1229	988	65.8	28.73	21.8	45
	6	8.7	4081	1093	1075	70.0	35.98	23.3	45
3	7	8.7	1960	1285	1078	66.3	69.80	60.8	53
	8	8.6	1736	916	1035	57.8	37.36	31.5	35
	9	8.6	2058	1245	935	65.0	43.75	38.3	43
4	10	8.6	2287	1657	1018	74.3	162.80	176.3	78
	11	8.3	2314	1242	1068	70.5	148.10	102.3	60
	12	8.5	2063	1033	1028	66.5	178.80	124.3	48

Total concentration of nickel in the examined samples in the range (1736; 4081) mg · $\mathrm{kg^{-1}}$ (Table 2). Most often reported admissible nickel content in soils used for forming purposes was 100 ppm [17]. According to Decree by Minister of the

Environment regarding soil quality standards and earth quality standards [18] industrial grounds or useful minerals grounds can contain maximum 300 mg Ni in kg of soil. In the soils formed from serpentine minerals nickel concentration reaches the values of thousand ppm [17]. Detected high range of total contents of nickel forms finds its confirmation in the results of examination conducted in the area of other serpentine dumping grounds subjected to investigation [19], as well as nickel ore mines connected with Lower Silesian occurrences of serpentine [20].

In the analyzed soil material there was also determined considerably high content of total chromium, ranging from 916 mg $\cdot$ kg^{-1} to 1657 mg $\cdot$ kg^{-1} – Table 2. For soils formed from serpentine minerals typical values range 5000 mg $\cdot$ kg^{-1} (0.5 %) Cr, at the range from 1000 mg $\cdot$ kg^{-1} to even 25000 mg $\cdot$ kg^{-1},which depends on the amounts of scattered chromite [21]. Polish soils, in relation to their mechanical composition, contain average from 7 ppm of chromium for light soils to 24 ppm for heavy soils [17]. The content of total manganese in soil samples from serpentine waste dump in Grochow amounted to (813; 1188) mg $\cdot$ kg^{-1} – Table 2. Average manganese content in sandy soils of Poland equals 240 ppm and in loamy soils it is about 570 ppm, while admissible content in cultivated soils is assumed as (1500; 3000) ppm Mn [17].

Soil samples collected from the waste dump contained elevated (as compared with average amounts in Polish soils) values of total cobalt, since they were found within the range of (57.8; 86.3) mg $\cdot$ kg^{-1} – Table 2. Detected Co concentrations exceeded admissible values for grounds used for farming purposes as the latter ones equal to 30 mg $\cdot$ kg^{-1} [17]. Yet the values obtained did not exceed admissible level of this chemical element for useful minerals grounds [18]. Concentrations of the remaining analyzed metals (Cu, Pb, Zn) met their natural level [17], except for the samples from stand No. 4 lead and copper contents featured slightly higher values.

The contents of soluble metals subjected to analysis, thus those of significant meaning as far as plants are concerned, proved that they constitute, except for nickel and manganese, only a small per cent of their total contents (Table 3). It was determined that concentration of nickel mobile forms ranged from 12.0 % to 25.8 % of total forms content, while in the case of available manganese it amounted from 20.5 % to 66.4 %. Concentrations of mobile forms of the remaining metals were as follows: cobalt (14.8; 24.4) mg $\cdot$ kg^{-1} and chromium (1.1; 10.8) mg $\cdot$ kg^{-1} (Table 3). The results obtained pointed to especially low quantity of chromium available for plants whose contribution does not exceed 1 % of total forms content. According to the literature [21], available forms of chromium in serpentine soils occur in extremely low quantities, which is expressed in scarce absorption of this metal by plants.

Our own investigation was carried out regarding four diversified fragments of serpentine dumping ground, which enabled their comparing with one another in the view of heavy metal content in the ground. Recorded total contents of selected heavy metals (Table 2) proved to be diversified and they depended both on the fragment of examined dumping ground and on chemical element analyzed.

As it results from the data of Table 3 showing the concentrations of mobile form of analyzed metals determined for particular stands, the stand No. 4 (typical dumping ground covered with poor vegetation) characterized (in the case of all the elements) the

Table 3

The content of soluble forms of selected heavy metals in soil collected from serpentine waste dump in Grochow

Stand	Sample number	Soluble forms content [mg · kg^{-1} of soil]						
		Ni	Cr	Mn	Co	Cu	Pb	Zn
1	1	600.5	1.3	244.0	15.8	3.29	11.7	15.5
	2	388.8	1.1	251.5	14.8	3.52	14.0	14.5
	3	353.1	1.9	305.0	17.3	4.73	19.7	27.0
2	4	425.9	5.2	644.5	26.1	11.13	6.4	10.0
	5	424.0	8.4	630.5	26.7	9.57	6.3	11.0
	6	488.7	7.6	622.0	28.3	10.61	6.7	11.0
3	7	465.8	6.0	659.0	24.4	60.33	39.0	17.0
	8	364.3	3.3	662.5	21.7	13.46	14.2	9.5
	9	500.1	7.5	620.5	28.3	22.93	20.8	12.5
4	10	573.7	10.8	648.5	27.8	42.73	132.5	27.5
	11	596.5	9.0	698.5	29.7	115.80	74.6	27.5
	12	448.0	6.4	632.0	24.0	95.30	76.3	14.0

highest values. The stand No. 1 featured the lowest contents of mobile chromium, manganese, cobalt and copper. The lowest concentrations of soluble lead and zinc were detected in detrial minerals originating from the stand No. 2. On the basis of the examinations conducted it is possible to state that soil pH amount from 7.4 to 8.7. Basic reaction constitutes a characteristic property of serpentine minerals formed from ultrabasic rocks [22].

The content of selected heavy metals in plants

Considerable accumulation of nickel in plants, ranging up to several thousands ppm Ni in dry matter can occur in some plant species growing on serpentine soils "nickel" ones [23]. Nickel concentrations, which can prove toxic, in plants ranges from 10 to100 ppm and they depend, among others, on plant resistance or chemical form of the element [17]. Analyzed parts of *Silene vulgaris* contained from 23.7 to 161.8 mg Ni in kg d.m., yet only two samples showed Ni concentration exceeding 100 mg · kg^{-1} d.m. (Table 4). The content of chromium in the analyzed plant material was fund within the range of 2.6–41.6 mg · kg^{-1} d.m. (Table 4). The value assumed as toxic for plants equals 20 ppm d.m. and it was exceeded in three samples. Chromium content in plants on serpentine waste dump in Grochow reached higher values than those detected on serpentine dumping ground in Wirki [10]. Sample analysis of *Silene vulgaris* showed manganese content meeting the range 49.6–127.7 mg · kg^{-1} d.m. (Table 4). Manganese concentration in plants most often amounts several tens ppm in dry matter, but it can range from several to even several thousands ppm Mn, according to plant species and properties of the ground [23]. Cobalt concentration in a plant was between 1.80–6.62 mg · kg^{-1} d.m. (Table 4). Natural Co content in plants is usually much lower than the one detected in the examined plant material [24]. Higher concentration of

Table 4

The content of selected heavy metals in *Silene vulgaris* from serpentine waste dump in Grochow

Stand	Sample number	Plant parts	Heavy metals content [mg · kg^{-1} d.m.]							
			Fe	Ni	Cr	Mn	Co	Cu	Pb	Zn
1	1	aboveground	938.0	60.5	5.7	60.5	2.94	5.32	6.70	22.45
	2		481.5	40.0	2.6	60.5	2.30	3.89	4.30	16.85
	3	underground	1056.5	63.0	7.2	77.6	3.34	32.65	7.00	32.35
2	4	aboveground	597.0	30.5	10.1	81.4	2.14	3.76	4.30	17.60
	5		453.0	23.7	5.4	78.2	1.96	4.81	4.50	21.65
	6	underground	1818.0	87.1	29.1	100.9	4.31	6.53	4.20	20.70
3	7	aboveground	829.5	47.4	10.5	62.4	2.56	7.70	7.65	18.60
	8		397.5	24.2	5.5	49.6	1.80	10.01	6.70	24.70
	9	underground	2892.0	159.2	41.6	122.2	6.01	29.05	15.90	23.65
4	10	aboveground	1488.0	88.0	16.1	70.0	3.68	15.97	7.80	15.00
	11		453.0	22.8	4.0	57.8	2.10	12.42	9.50	9.14
	12	underground	3011.5	161.8	37.1	127.7	6.62	25.89	21.30	24.88

cobalt can be explained by absorption of this element in the amounts proportional to its soluble forms occurring in the ground [17]. Assumed toxic level for plants is higher than 15–50 ppm [17]. Concentrations of the remaining heavy metals (Cu, Pb, Zn) remained within their natural range or even relatively low, in the case of zinc [17]. Elevated concentrations of nickel, chromium and cobalt in plants can be justified by the character of serpentine ground, which was rich in those elements [2, 25]. The estimation of heavy metals in above- and underground parts of plants makes it possible to state that plant roots accumulated markedly higher quantities of analyzed elements (Table 4). The tendency in plants to accumulate metals in underground parts protects plants organs important for their functioning (flowers, fruits), yet it is not a rule governing plants higher tolerance of excessive amounts of metals [26].

Conclusions

1. There were designated 30 species of vascular plants on serpentine waste dump in Grochow.
2. Most numerously represented botanical families were Poaceae, Fabaceae and Asteraceae.
3. There were recorded high contents of total form so Ni, Cr, Mn and Co (as compared with a natural one) in soil material originating from serpentine waste dump.
4. Soluble forms of analyzed metals (generally) provided for only an insignificant per cent of their total forms.
5. In plant material (*Silene vulgaris*) coming from serpentine waste dump there were recorded high concentrations of Ni, Cr and Co in comparison with natural ones. In all the examined plants concentrations of the metals examined were higher in underground plant parts than in aboveground parts.

6. The reaction of soil material subjected to examination, collected from serpentine dumping ground was basic.

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AKUMULACJA METALI CIĘŻKICH PRZEZ *Silene vulgaris* WYSTĘPUJĄCEJ NA HAŁDZIE ODPADÓW SERPENTYNITOWYCH W GROCHOWIE (DOLNY ŚLĄSK)

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Abstrakt: Badaniami objęto hałdę odpadów serpentynitowych w Grochowie (Dolny Śląsk). Skład florystyczny analizowanego zwałowiska był ubogi. Na badanych powierzchniach stwierdzono jedynie 30 gatunków roślin naczyniowych, należących głównie do trzech rodzin botanicznych – Poaceae, Fabaceae, Asteraceae.

Gatunkiem dominującym na zwałowisku w Grochowie był jedyny rozpoznany na jego obszarze przedstawiciel Caryophyllaceae – *Silene vulgaris.* Analiza materiału glebowego wykazała, że ogólne zawartości niklu, chromu, manganu i kobaltu były wyższe od przeciętnych ilości tych metali w środowisku glebowym.

Formy mobilne, dostępne dla roślin stanowiły we wszystkich przypadkach tylko niewielki procent ich form całkowitych. W materiale roślinnym pochodzącym ze zwałowiska stwierdzono wysokie w porównaniu z naturalnymi zawartości Ni, Cr i Co. Koncentracje wszystkich analizowanych metali były wyższe w częściach podziemnych *Silene vulgaris* niż w częściach nadziemnych.

Słowa kluczowe: metale ciężkie, hałda, serpentynit, *Silene vulgaris*

DOI: 10.2428/ecea.2012.19(04)044 ECOL CHEM ENG A. 2012;19(4-5):421-431

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IMPACT OF TAXONOMIC STRUCTURE AND BENTHIC FAUNA BIOMASS ON THE BIOLOGICAL CLASSIFICATION OF RIVER WATERS

WPŁYW STRUKTURY TAKSONOMICZNEJ I BIOMASY FAUNY BENTOSOWEJ NA BIOLOGICZNĄ KLASYFIKACJĘ WÓD RZECZNYCH

Abstract: The study results presented include an analysis of the biological material and benthic sediments collected in 2007 from four streams located in the Oder River basin. These served as the basis for determining the taxonomic structure and biomass of macrobenthos at the sampling sites as well as of the water quality based on the Biological Monitoring Working Party index adapted for Poland (BMWP-PL). The streams studied varied with regard to the qualitative and quantitative structures of individual taxa, and the biodiversity in the streams was very high. Insecta was the dominant in terms of numbers in all of the streams studied, and among them Trichoptera was the most frequently occurring group of organisms. The macrozoobenthos biomass values from 66 to 252 $g \cdot m^{-2}$ might indicate that the biological capabilities of these streams are high. The BMWP-PL index evaluation system indicates that the studied streams can, in most instances, be classified as either marginally polluted or polluted (water quality classes III and IV).

Keywords: macrozoobenthos, domination structure, biomass, BMWP-PL index, lowland streams

Introduction

Many variables, including bottom type, water flow, temperature, and physico-chemical factors, can influence the richness of organisms in a given basin [1–2]. These factors and many others are largely responsible for the composition and density of

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benthic macrofauna in any body of water [2–4]. Evaluating biodiversity requires knowledge of the characteristics of three structural components of the aquatic biocenosis: species richness (which is the number of species that occur), domination structure, and density. As an example, the natural biocenosis of a stream that is not subjected to transformation is characterized by high species richness, evenly distributed individuals among species, and low to moderate abundance [5]. Pollution can lead to a decline in species richness, and in some cases this can be reduced to a single species that is capable of tolerating extreme environmental conditions. River biocenosis subjected to anthropogenic pressure exhibit continually diminishing biodiversity. It should also be borne in mind that all polluted environments are characterized by low biodiversity. Moderate pollution, on the other hand, can contribute to an initial increase in the number of taxons and a more even distribution among individuals, and consequently, in increased index values. Studies with the aim of reviewing all the groups occurring in a given stream as well as determining their biomass and density are conducted infrequently because of insufficient knowledge of the taxonomy of many groups and the intensive labor required of such undertakings. Detailed studies of single taxonomic groups are more common [5–6], and a range of indexes are used to calculate biodiversity [6]. These are used to determine the reaction of the structure of the entire assemblage of organisms, but without taking into consideration the reaction of indicator species. The use of biodiversity indexes is also burdened with other limitations. Their values fluctuate depending on when and how sampling is performed taking into consideration the different taxonomic and morphological-hydrological characteristics of the stream being studied [5, 7, 8].

The aim of the study presented in this article was to trace the quantitative and qualitative density and biomass of benthic fauna depending on the location of occurrence and their impact on the quality classification of stream waters through the use of biological indexes. The study was performed in four streams in the lowlands of the Oder River basin in northeastern Poland.

Materials and methods

The study was conducted on four streams (Wolczenica, Krapiel, Ina, Rurzyca) that are right-bank tributaries of the Oder River (Fig. 1). The samples were collected from May to June 2007 at sampling sites distributed from the stream sources to their mouths. The study was conducted as part of project entitled "Determining the biomass of benthic fauna in selected streams in Western Pomerania and determining the water quality of them based on the BMWP-PL (*Biological Monitoring Working Party* adapted for Poland) index in order to estimate the food base for fish". The project number is OR16-61535-OR1600014/07, and funding was obtained from the Sectoral Operational Programme "Fisheries and Fish Processing 2004–2006".

Benthic fauna samples were collected using a special bottom scraper with a square-shaped intake measuring 0.25 × 0.25 m along bottom segments 1 m in length. This permitted reporting results on both the quality and quantity of the samples. After the biological material was transported to the laboratory, it was sifted on sieves with a mesh

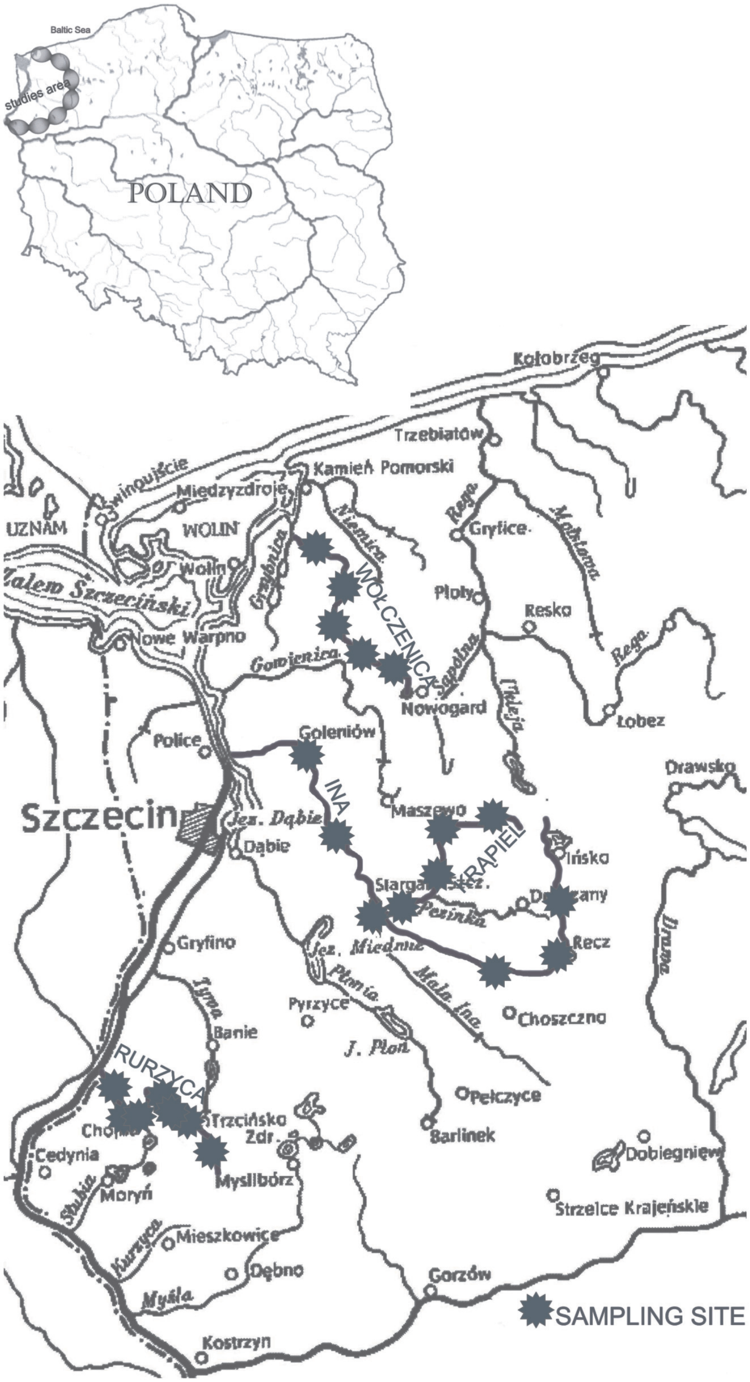

Fig. 1. Location of the surveyed streams drainages and location of sampling sites

bar length of 0.45 mm, placed in containers and preserved with 40 % alcohol. A Nikon stereo microscope was used to identify the material for quality analyses. Then the sorted material was weighed on a Radwag analytical scale to the nearest 0.01 mg.

The density of organisms per 1 m^2 of bottom area (N) was calculated with the following formula:

$$N = n / a \ [\text{indiv.} \cdot \text{m}^{-2}]$$

where : n – number of organisms in the sample,
a – surface area of collection site = length of scraper side × length of sampled segment = 0.25 × 1.00 m = 0.25 m^2.

Biomass (B) was also calculated per 1 m^2 according to the following formula:

$$B = b / a \ [\text{g} \cdot \text{m}^{-2}]$$

where: b – weight of individual in the sample [g],
a – sampling surface area = 0.25 × 1.00 = 0.25 m^2.

The results obtained were processed statistically and correlation coefficients were determined among sampling sites and the density and biomass of the organisms.

The results of the benthic fauna studies were also used to determine the water quality of the streams using two criteria: the value of the BMWP-PL index and the value of the biodiversity index [9, 10]. The values of the indexes were obtained by adding points for the families of the macrofauna (from 1 to 10 depending on their sensitivity to pollution) occurring at the various sampling stations, and then the results were verified with the biodiversity index. The final result was the basis for classifying the waters in one of the five water purity classes (I – very clean; II – clean; III – marginally polluted; IV – polluted; V – heavily polluted).

Results and discussion

The fauna density in all streams studied was 10132 individuals per 1 m^2, at a total biomass of 451.7 $g \cdot m^{-2}$. The highest density of benthic organisms (4112 $\text{indiv.} \cdot m^{-2}$) and the highest biomass (252.5 $g \cdot m^{-2}$) was noted in the Rurzyca River. The values of these in the other streams were as follows: 2628 $\text{indiv.} \cdot m^{-2}$ and 45.4 $g \cdot m^{-2}$ in the Ina River; 1660 $\text{indiv.} \cdot m^{-2}$ and 66.4 $g \cdot m^{-2}$ in the Wolczenica River; 1732 $\text{indiv.} \cdot m^{-2}$ and 87.5 $g \cdot m^{-2}$ in the Krapiel River (Table 1). An interesting situation was noted in the Ina River, where a large number of organisms had the minimum biomass values. The reason for this is found in the quantitative structure of the organisms comprising the benthic fraction: of the 2628 $\text{indiv.} \cdot m^{-2}$ noted, 576 $\text{indiv.} \cdot m^{-2}$ were Oligochaeta with a biomass of just 0.6 $g \cdot m^{-2}$; 652 indiv./m^2 were Diptera with a biomass of 0.1 $g \cdot m^{-2}$; 588 $\text{indiv.} \cdot m^{-2}$ were Gammaridae with a biomass of 1.1 $g \cdot m^{-2}$; 460 $\text{indiv.} \cdot m^{-2}$ were mussels from the family Sphaeridae with a biomass of 2.7 $g \cdot m^{-2}$. However, Trichoptera, with only 76 $\text{indiv.} \cdot m^{-2}$ had a biomass of 35.5 $g \cdot m^{-2}$, which represented nearly 80 % of the biomass of all organisms noted in this stream.

Table 1

Density, biomass and correlation coefficients of selected parameters studied streams

Factor	Wolczenica	Ina	Kapiel	Rurzyca
Density of macroinvertebrate [indiv. · m^{-2}]	1660	2628	1732	4112
Biomass of macroinvertebrate [g · m^{-2}]	66.4	45.4	87.5	252.5
Correlation coefficient between study sites and the density of macroinvertebrate	0.05	0.06	0.03	0.57
Correlation coefficient between study sites and the biomass of macroinvertebrate	0.26	0.08	0.01	0.59

The area studied was characterized by a high degree of taxonomic diversity among macroinvertebrates. The benthic organisms noted in the material analyzed were represented by 6 invertebrate classes (Fig. 2): Hirudinea, Crustacea (Amphipoda and Isopoda), Arachnida, Insecta (Ephemeroptera, Coleoptera, Odonata, Trichoptera, Heteroptera, Diptera, Megaloptera, Lepidoptera), Gastropoda and Bivalvia. Macroinvertebrate taxa found in the studied rivers are typical of many lowland rivers of Poland. A similar taxonomic composition was noted by Krolak and Korycinska [2] in the Liwiec River. The biomass dominants throughout all the streams were Insecta, while the co-dominants were Gastropoda and Bivalvia (Fig. 2). Among Insecta, the dominating group by weight was the caddisfly (Trichoptera) (Fig. 3). Krolak et al [11] and Zasepa et al [1] reported similar results. The distribution of benthic fauna biomass was slightly different in each of the streams. While the dominant was Insecta at most of the stations in three streams (Wolczenica, Krapiel, Ina), its domination was linked to the occurrence and dominating biomass of the caddisflies (Fig. 2–3). The exception was station 5 in the Wolczenica River, where the dominant was Diptera (Fig. 2–3), similarly to the studies by Bylak and Kukuly [12]. According to these authors, the rock fraction of the stream bottom played a decisive role in determining the domination structure. The bottom structure might also have played a role in determining the biomass of Diptera in the Wolczenica; the current author's own studies indicate that the dominant fraction here was fine-grained gravel of 4 mm. On the other hand, in the Rurzyca River, Trichoptera (and with this Insecta itself) dominated by weight only at site 6, while at sites 1 and 2 it was a subdominant. However, at the remaining sites it dominated by weight over either molluscs or crustaceans (Fig. 2–3). It is also of note that the highest Gastropoda biomass was recorded in the lower segments of the studied streams and in the source segment of the Rurzyca River. These situations could have been because of a lack of suitable environmental conditions at a given study station or because of periodic changes in conditions, which is noted distinctly in the study by Flecker and Feifarek [13] and Sawa and Popek [14]. The analysis of the degree of linear dependence between organism biomass and study station indicated there was a weak dependence between these variables in the Rurzyca River ($r = 0.59$), but no such dependence was noted in any of the other streams (Table 1).

The taxonomic structure and percentage share of the various benthic fauna classes was somewhat different in comparison with biomass (Fig. 2). Insecta dominated

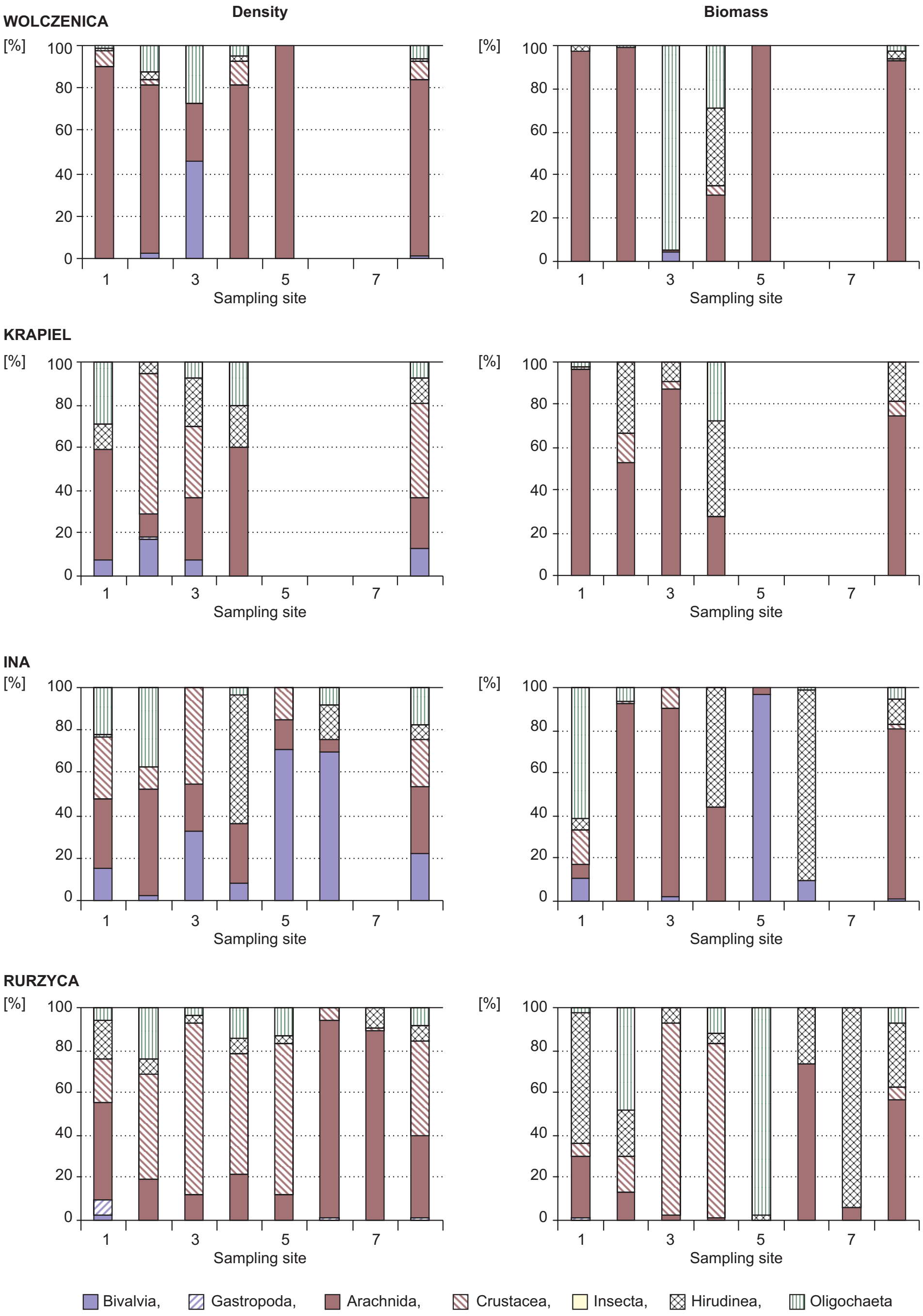

Fig. 2. Percentage of density and biomass invertebrate benthic fauna of selected streams (Wolczenica, Krapiel, Ina, Rurzyca)

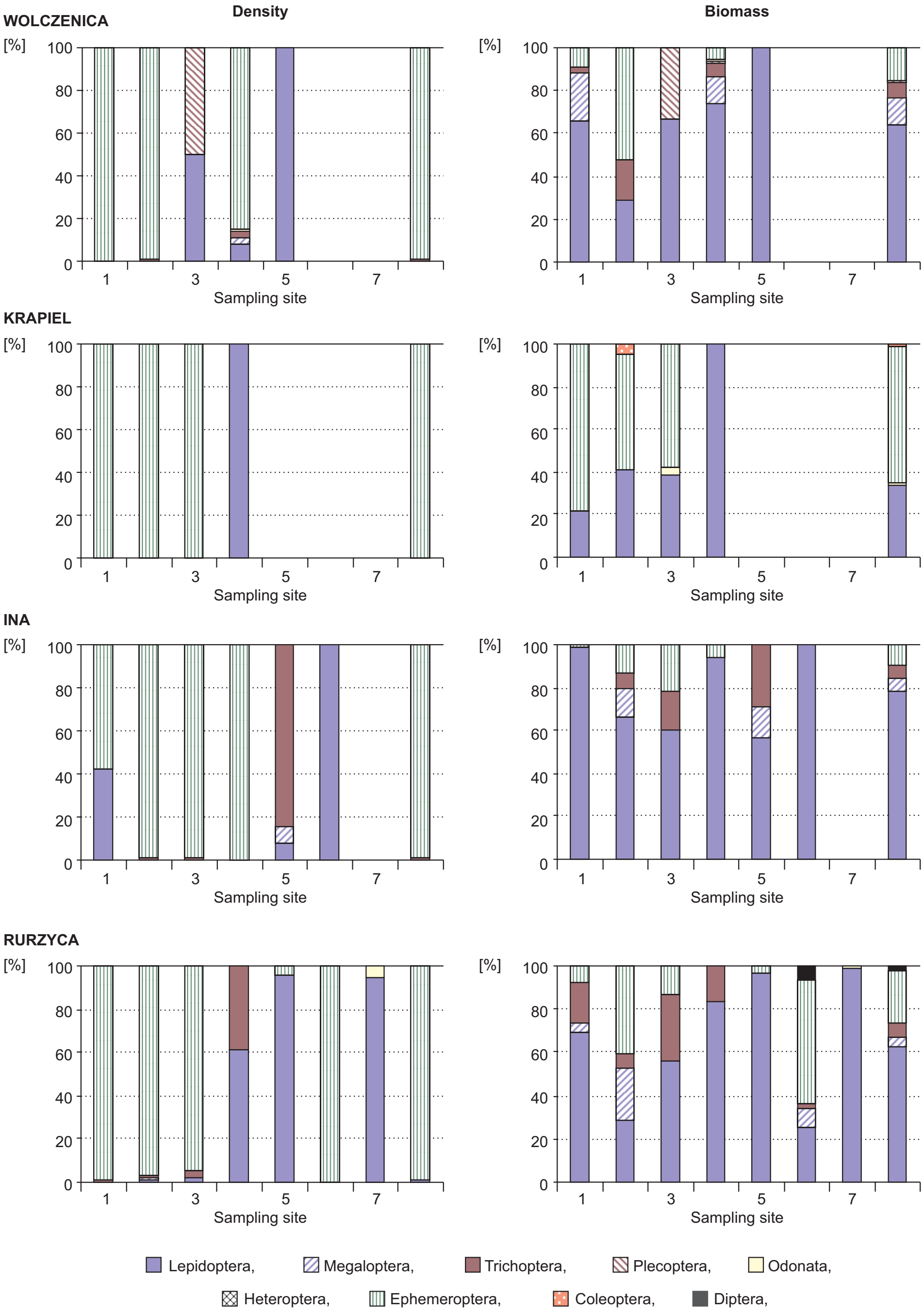

Fig. 3. Percentage of density and biomass among insects of selected streams (Wolczenica, Krapiel, Ina, Rurzyca)

quantitatively at most stations only in the Wolczenica River, while the highest density was noted for Diptera (Fig. 2–3). In the other streams, Insecta dominated quantitatively only at 2 or 3 sampling stations (which was also mainly due to the domination of Diptera, while there were greater numbers if specimens noted among Crustacea and Mollusca (Fig. 2–3). Only at two stations in the Rurzyca River was a dependence noted between the density and the biomass of the organisms; even so, the highest density and biomass were achieved by Crustacea at stations 3 and 4 (Fig. 2, Table 1). A weak degree of linear dependence between density and sampling station was also noted in the Rurzyca River (Table 1).

Benthic fauna is one of the most frequently used bioindicators applied during studies of the water quality of river environments [15], but the BMWP-PL index has been tried and tested under Polish conditions, and it is considered by many authors to be among the best [2, 11, 16–18]. This is because some of the species included in its list meet all the requirements above for being so-called “ideal indicator organisms”. The organisms among them that are not highly mobile are good indicators of local water states, while mobile species are good indicators of water quality over longer stretches of river. The domination structure in the studied streams should influence the evaluation of water quality assessed with biotic indexes since the assumption is that the occurrence or lack of certain organisms can reflect changes in the aquatic environment. The density of the benthic fauna and its biomass do not influence water classifications. In marginally polluted water, the numbers of Ephemeroptera, Trichoptera, and other species requiring clean water decline, while the numbers of Oligochaeta increase [9–11]. Since at most of the stations in the streams studied the dominant organisms were from the orders Trichoptera or Crustacea (Fig. 1–2) (of which 90 % were Gammaridae), which are characteristic of either clean or marginally polluted waters, then the water classification should be in either quality class II or III. The classification made using the criteria of the BMWP-PL index, however, was lower and water quality classes III and IV were generally more prevalent (Table 2).

The waters of the Rurzyca, Krapiel, and Ina rivers were classified in their various segments from clean water (class II) to marginally polluted (class IV) (Table 2). According to biological criteria, the quality of Wolczenica River waters at the sampling site near the mouth was site was heavily polluted (class V) (Table 2). Similar dependencies were reported by Krolak et al [11, 19]. Biodiversity and domination structure also have a significant impact on quality assessments. Several species, or groups of organisms, usually co-dominate in clean streams. As the aquatic environment changes in response to pollution, the number of dominant species, or groups, usually decreases [20]. This occurred in the streams studied when the domination of one or two groups lowered the biodiversity indicator, and, along with it, the water classification category. In places where there was no clear dominant in terms of density, for example in the Wolczenica (sampling site 4), Rurzyca (sampling sites 1, 2), Krapiel (sampling site 3), or Ina rivers (sampling site 4), the biodiversity coefficient increased, and, thus, the water quality classification was higher (class II quality) (Table 2). Since according to the BMWP-PL point scoring system Oligochaeta and the larvae of the family Chironomidae from Diptera are awarded only three points, the occurrence of these

Table 2

Water quality at particular stream study sites as assessed with biological methods

Sampling sites	1	2	3	4	5	6	7
Wolczenica							
Total points BMWP-PL	68	33	14	78	7		
Water quality class by BMWP-PL	III	IV	IV	II	V		
Biodiversity index – "d"	4.56	2.79	2.43	4.46	1.22		
Water quality class by biodiversity index "d"	II	III	IV	II	IV		
Water quality class by biological assessment (total "BMWP-PL" and "d"')	III	IV	IV	II	V		
Ina							
Total points BMWP-PL	35	70	43	46	24	25	
Water quality class by BMWP-PL	IV	II	III	III	IV	IV	
Biodiversity index – "d"	2.71	4.27	2.97	4.65	2.16	2.76	
Water quality class by biodiversity index "d"	III	II	III	II	IV	III	
Water quality class by biological assessment (total "BMWP-PL" and "d"')	IV	II	III	III	IV	IV	
Krapiel							
Total points BMWP-PL	31	54	76	11			
Water quality class by BMWP-PL	IV	III	II	IV			
Biodiversity index – "d"	2.80	4.06	5.56	2.31			
Water quality class by biodiversity index "d"	III	II	I	IV			
Water quality class by biological assessment (total "BMWP-PL" and "d"')	IV	III	II	IV			
Rurzyca							
Total points BMWP-PL	97	67	47	35	45	62	31
Water quality class by BMWP-PL	II	III	III	IV	III	III	IV
Biodiversity index – "d"	7.42	4.59	3.44	3.44	3.04	4.01	2.56
Water quality class by biodiversity index "d"	I	II	III	III	III	II	III
Water quality class by biological assessment (total "BMWP-PL" and "d"')	II	III	III	IV	III	III	IV

Legends: I – very clean; II – clean; III – marginally polluted; IV – polluted; V – heavily polluted.

organisms in streams led to a decreased classification category. The family Chironomidae is the worst indicator of pollution since the qualitative difference in their occurrence between clean and polluted streams is not pronounced [21, 22]. Similar dependencies were reported by Raczynska and Raczynski [23].

Conclusions

1. In all of the streams studied, Insecta and Mollusca dominated in terms of weight. Among the former, Trichoptera was dominant, and only in one instance (Wolczenica River) did Diptera dominate.

2. The analysis of the biomass distribution along the courses of the studied streams indicated that Insecta achieved the highest biomass values in the Wolczenica, Karpiel, and Ina rivers, while Crustacea and Mollusca did so in the Rurzyca River.

3. The domination structure of benthic fauna in terms of density did not correspond to that of biomass since Crustacea or Insecta dominated at most of the study sites.

4. According to biological criteria, at most of the sampling sites the waters of the streams surveyed were either marginally polluted (water quality class III) or polluted (water quality class IV), which was indicated by the low numbers of co-dominants.

5. Only on the Rurzyca River was a weak dependency between benthic macroinvertebrate density and study site confirmed.

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WPŁYW STRUKTURY TAKSONOMICZNEJ I BIOMASY FAUNY BENTOSOWEJ NA BIOLOGICZNĄ KLASYFIKACJĘ WÓD RZECZNYCH

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Abstrakt: Przedstawione wyniki badań obejmują analizę materiału biologicznego i osadów dennych uzyskanych z czterech cieków dorzecza Odry prowadzonych w 2007 r. Na tej podstawie określono strukturę taksonomiczną fauny makrobentosowej i jej biomasę w miejscu pobierania próbek, a także dokonano klasyfikacji wód na podstawie wskaźnika BMWP-PL. Badane rzeki charakteryzowała zróżnicowana struktura jakościowa i ilościowa poszczególnych taksonów, a bioróżnorodność w badanych rzekach była bardzo duża. Pod względem ilościowym we wszystkich badanych rzekach dominowały Insecta, a wśród nich – Trichoptera jako najczęściej występująca grupa organizmów. Wartości biomasy makrozoobentosu (od 66 do 252 $g \cdot m^{-2}$) świadczyć mogą o wysokiej zdolności biologicznej tych cieków. System oceny indeksu BMWP-PL wskazuje, że badane rzeki można zaliczyć w większości przypadków do wód słabo zanieczyszczonych i zanieczyszczonych (III i IV klasa).

Słowa kluczowe: makrobentos, struktura dominacji, biomasa, indeks BMWP-PL, cieki nizinne

DOI: 10.2428/ecea.2012.19(04)045 ECOL CHEM ENG A. 2012;19(4-5):433-440

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SEASONAL CHANGES IN CHROMIUM CONTENT IN THE WATER OF THE BYSTRZYCA RIVER (DOLNOSLASKIE PROVINCE)

SEZONOWE ZMIANY ZAWARTOŚCI CHROMU W WODZIE RZEKI BYSTRZYCY (WOJEWÓDZTWO DOLNOŚLĄSKIE)

Abstract: The study was conduct on the Bystrzyca river and its tributaries. The samples water were tested for chromium(VI). Chromium content in the waters covered by the study corresponded to that characteristic of surface waters in the areas of Poland with medium chromium pollution levels. Locally recorded higher concentrations were probably a result of discharges of municipal sewage or sewage from small industrial plants.

Keywords: chromium, water rivers

Introduction

Water reservoirs in Poland are exposed to the effects of pollution, which comes in the form of waste and sewage from land and waters located in river catchment basins. One of the reasons for discharging chemical compounds and toxic substances into waters are poorly developed, inadequate or obsolete sewerage systems in many towns and cities. Another factor is the recreational use of lakes, ponds, rivers and neighbouring areas. Unfortunately, as yet Poland has not fully managed to link recreation with the presence of sanitary facilities.

The type of agricultural animal and plant production that is predominant in Poland has an adverse effect on water reservoirs and their catchment basins. The main cause of this phenomenon is inappropriate and often ill-considered use of natural and artificial fertilizers. A big problem is the use of crop protection chemicals for agricultural production. The compounds used for the purpose contain considerable amounts of heavy metals, which are very harmful to the entire ecosystem. Their accumulation in the food chain starts in water.

Many groups of chemical compounds are to be found in the natural environment. They are present in atmospheric air, soil and water. An important place among them is

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occupied by heavy metals, including chromium. Chromium is a rare metal. Its content in Earth's crust amounts to 0.037 %. Chromium has numerous applications in industry, *eg* it is used for plating metal objects, making iron alloys, producing pigments, manufacturing fungicidal compounds, in the dyeing industry, in construction as a mortar component, for making gels and glues, in the tanning and textile industries. It also enters the environment when coal is burnt [1].

The harmful effects of chromium depend on its valency, solubility and the way in which it is delivered. Chromium(VI) is more toxic than chromium(III). Chromium(VI) compounds are strong oxidizers, and so they irritate the respiratory track, damage the senses of taste, smell and hearing, harm the heart and the nervous system, and in the case of direct contact they cause ulcerations and poisonings. Potable water should not contain more than 0.05 $\mathrm{mgCr \cdot dm^{-3}}$ [2]. Chromium is harmful to fish in surface water when its content amounts to 15–80 $\mathrm{mgCr \cdot dm^{-3}}$, and to other aquatic organisms – from 0.08 to 10 $\mathrm{mgCr \cdot dm^{-3}}$ [3].

Because chromium is present in surface waters and is toxic, and because water is drawn from the dam reservoir at Lubachow for drinking by people, it was decided to determine chromium content in the water of the Bystrzyca River and its tributaries, which are the main sources of water flowing into the reservoir.

Materials and methods

The Bystrzyca River is a left-bank tributary of the Odra. It is 95.2 km long. Its direct catchment basin is made up by mountains, rocky terrain, afforested areas, and recreational areas. The river starts in the Kamienne Mountains near the town of Gluszyca, or more exactly near the town of Wrzesnik, where a trachyte quarry is located. In the nearby village of Bartnica there is Rock Materials Plant 'Bartnica', which is a source of large amounts of dust, which is later to be found around the Zloty Potok River, the first of the Bystrzyca tributaries. Other tributaries, *ie* the Otluczyna, Zlota Woda, Potok Marcowy Duzy, Rybna, Jaworzynik and Walimianka, mainly collect urban and industrial waste. The Rybna River joins the Bystrzyca at the town of Gluszyca, and the Jaworzynik and Walimianka Rivers at the village of Jugowice. Two dam reservoirs have been built on the Bystrzyca River: the first one 47.00 km from its source, at the village of Mietkow, the other one – at 75.00 km – at the town of Lubachow.

The study was conducted on the Bystrzyca River, which feeds the reservoir, and its upstream tributaries. The following sampling sites were selected: on the Bystrzyca River just below its source, on the Zloty Potok, Otluczyna, Potok Marcowy Duzy, Zlota Woda, Rybna, Jaworzynik, Walimianka, the Bystrzyca before the Lubachow reservoir, the Bystrzyca 100 m below the dam. The study material was collected in 2007 in periods in which the water quality is known to change: in spring, summer, autumn and winter, by means of a 2 $\mathrm{dm^3}$ water sampler.

The samples were tested for chromium content. Mineralization was done with concentrated nitric acid. Chromium content was determined using *atomic absorption spectrophotometry* (AAS) by means of a Spectr AA-110/220 unit.

Results

Bystrzyca river tributaries

In spring chromium content ranged between 0.0001 mgCr · dm^{-3} in the Zloty Potok and Jaworzynik to 0.0003 mgCr · dm^{-3} in the Zlota Woda (Fig. 1). The average chromium content in spring was 0.0002 mgCr · dm^{-3}. The average chromium content in the Bystrzyca tributaries in summer amounted to 0.0009 mgCr · dm^{-3}. The maximum value was recorded for the Potok Marcowy Duzy (0.0023 mgCr · dm^{-3}) (Fig. 2). No

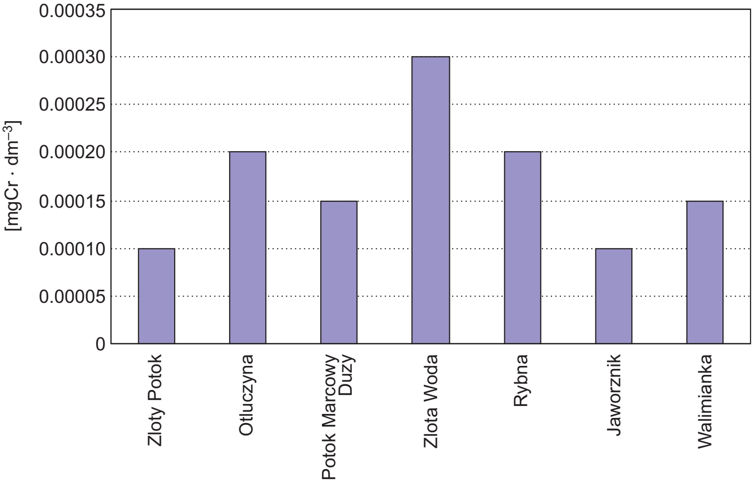

Fig. 1. Chromium [mgCr · dm^{-3}] in water of the Bystrzyca river tributaries – spring 2007

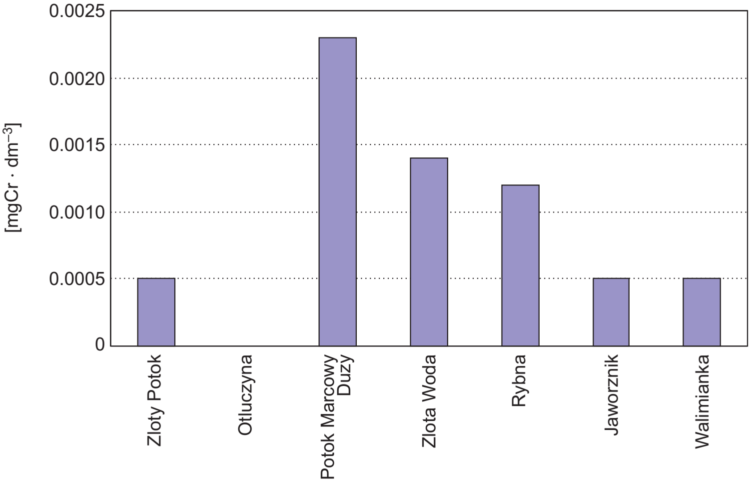

Fig. 2. Chromium [mgCr · dm^{-3}] in water of the Bystrzyca river tributaries – summer 2007

chromium was found in the Otluczyna River water. No chromium was also found in the autumn in the water samples taken from the rivers Otluczyna, Potok Marcowy Duzy, Rybna and Jaworzynik. The highest concentration, at 0.0010 mgCr · dm^{-3}, was measured for the Walimianka River (Fig. 3). The average chromium content in the Bystrzyca tributaries amounted to 0.0003 mgCr · dm^{-3}. The maximum winter content, at 0.0008 mgCr · dm^{-3} was determined for the water samples from the Jaworzynik River (Fig. 4). Just like in autumn, no chromium was found in four tributaries (Zloty Potok, Otluczyna, Potok Marcowy Duzy, Walimianka). The average chromium content was 0.0002 mgCr · dm^{-3}.

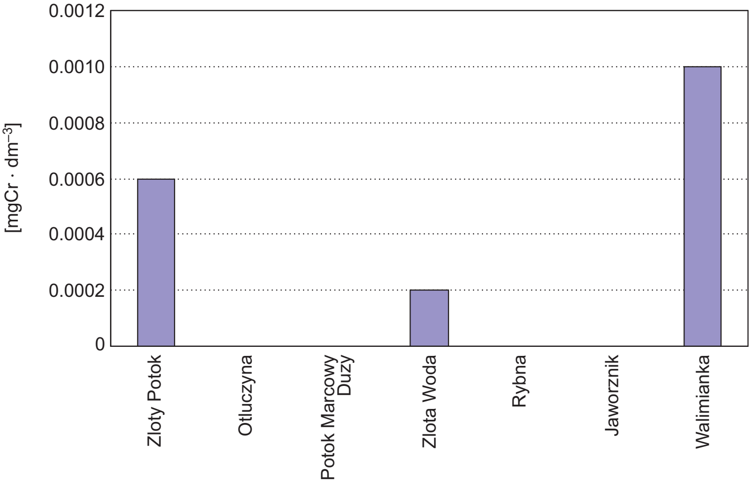

Fig. 3. Chromium [mgCr · dm^{-3}] in water of the Bystrzyca river tributaries – autumn 2007

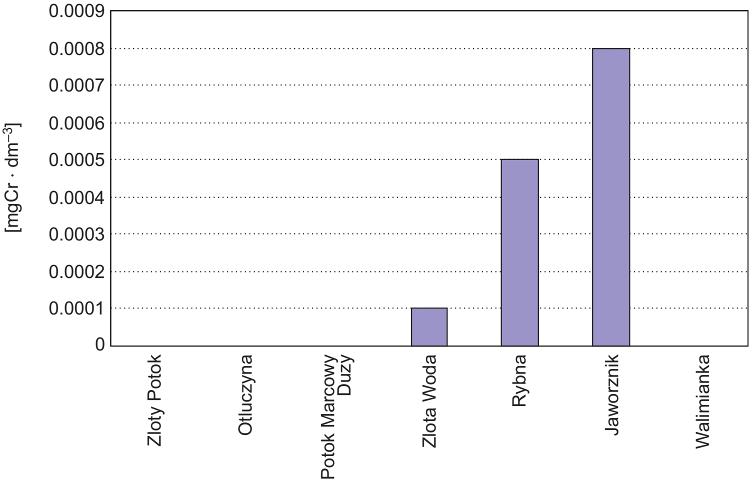

Fig. 4. Chromium [mgCr · dm^{-3}] in water of the Bystrzyca river tributaries – winter 2007

Bystrzyca river

Chromium concentrations in the Bystrzyca River water at the site below the source above the village of Bartnica were high in summer and in autumn. They reached their maximum value in autumn – 0.0019 mgCr · dm^{-3} (Fig. 7). In winter and in summer they were much lower, at 0.0000 mgCr · dm^{-3} and 0.0001 mgCr · dm^{-3}, respectively (Fig. 5, 6). In the samples from the Bystrzyca taken at its inflow into the Lubachow reservoir the highest metal content was recorded in winter (0.0029 mgCr · dm^{-3}) (Fig. 8). In autumn and summer the figures were significantly lower, at 0.0010 mgCr · dm^{-3} in autumn and 0.0009 mgCr · dm^{-3} in summer (Fig. 6, 7). The water flowing from the Lubachow reservoir in summer had the highest chromium content (0.0031 mgCr · dm^{-3}) (Fig. 6). The autumn samples had over four times less chromium (Fig. 7). In winter and autumn more chromium was retained in the dam reservoir reservoir (Fig. 7, 8). There were no significant changes in spring. In summer much more chromium flowed out of the reservoir than into it.

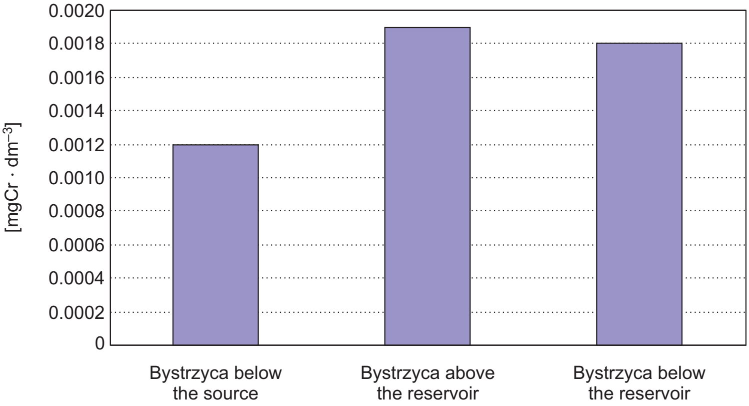

Fig. 5. Chromium [mgCr · dm^{-3}] in water of the Bystrzyca river – spring 2007

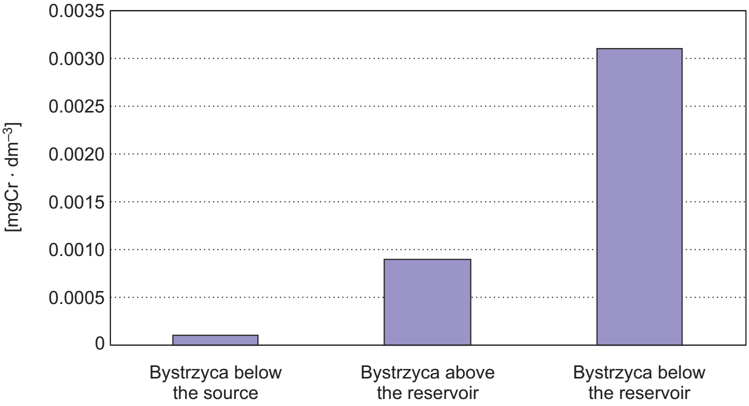

Fig. 6. Chromium [mgCr · dm^{-3}] in water of the Bystrzyca river – summer 2007

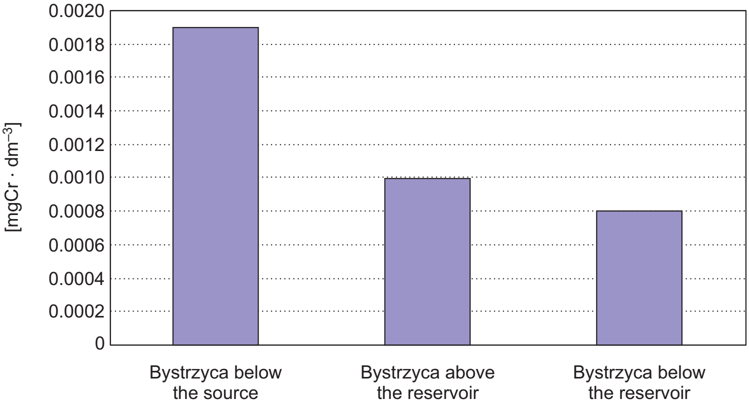

Fig. 7. Chromium [mgCr · dm^{-3}] in water of the Bystrzyca river – autumn 2007

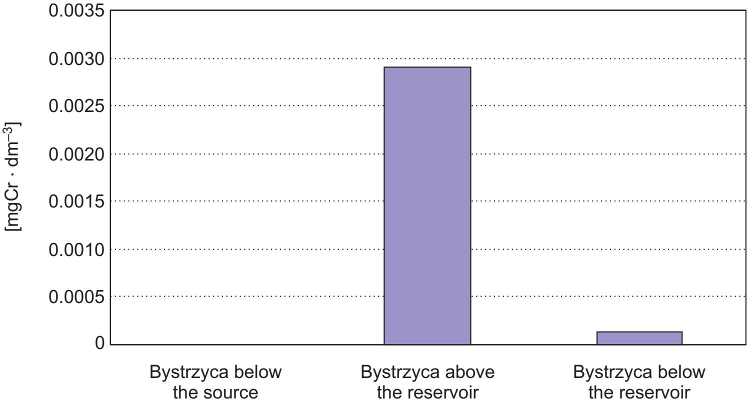

Fig. 8. Chromium [mgCr · dm^{-3}] in water of the Bystrzyca river – winter 2007

Discussion

The Bystrzyca River and its tributaries between their sources and the Lubachow reservoir are mountainous or foothill in nature. The water flow is thus rather fast and any pollutants discharged in the catchment basin are quickly carried by the river and reach the reservoir. Most pollution in the catchment comes from urban sewage. Industrial pollution occurs rarely. It is rather insignificant and principally originates from small plants located at the town of Gluszyca or the village of Jugowice, which are ‘household’ processing plants or repair shops. Most probably chromium in the waters of the Bystrzyca catchment comes from compounds formed as a result of burning coal in household stoves. The pollutants then fall as dry or wet deposition within the catchment basin.

The amounts of chromium in the water samples from the Bystrzyca and its tributaries were within the average amounts determined for waters in Poland (0.0030; 0.0060) mg

Cr · dm^{-3} and in most cases did not exceed 0.0050 mgCr · dm^{-3} [4]. The maximum figure measured for the Bystrzyca (0.0052 mgCr · dm^{-3}) was at a similar level.

According to a report on the environment in Dolnośląskie province in 2007, the Bystrzyca River belongs to waters with light and medium pollution levels (class II and water cleanliness categories A1 and A2) [5]. Water quality is adversely affected by bacteriological pollution, which was not, however, covered by the study in question. Based on the chromium content only, the waters investigated may be classified as class A1 and surface water cleanliness class I [6, 7].

Analyses of chromium contents in flowing waters in Europe and in other parts of the world have shown amounts of the metal similar to those in the Bystrzyca. The amounts for such waters ranged from 0.0001 mgCr · dm^{-3} to 0.0041 mgCr · dm^{-3} [8–11].

Slightly higher contents were found in the Nysa Szalona and its tributaries joining the river above the dam reservoir Slup. The chromium content in the catchment basin of the river, which flows through Dolnoslaskie province, just like the Bystrzyca, oscillated between 0.0016 mgCr · dm^{-3} and 0.0096 mgCr · dm^{-3} [12].

Chromium levels much higher than those in the Bystrzyca have been found in surface waters flowing from urban waste landfills in Wroclaw, where they fell within the range of (1.25; 9.0) mgCr · dm^{-3} [13]. High amounts of chromium have also been found in the water in the settling tanks at the dust disposal site of Elektrocieplownia Wroclaw (Cogeneration Plant Wroclaw) in Kamien near Wroclaw (0.05 mgCr · dm^{-3}) and in the ditch behind the tanks, which carries water to the Topor River (0.03 mgCr · dm^{-3}) [14]. High amounts of cadmium were also found in rivers in Germany and Turkey (0.003; 0.0668) mgCr · dm^{-3} [9, 15].

Conclusions

The waters of the Bystrzyca and its tributaries flowing into the Lubachow reservoir are characterized by medium pollution with chromium. Locally measured higher concentrations were probably a result of discharges of urban sewage or sewage from small industrial plants. The 1990s saw the closure of textile and clothing plants in the Bystrzyca catchment basin at the village of Walim and the town of Gluszyca. The sewage discharged into surface waters contained significant amounts of cadmium compounds. Apart from some negative aspects of the phenomenon (unemployment and impoverishment), there is also a positive side to it – an improvement in the condition of the natural environment. The Bystrzyca water is now definitely cleaner (even by up to two cleanliness classes).

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SEZONOWE ZMIANY ZAWARTOŚCI CHROMU W WODZIE RZEKI BYSTRZYCY (WOJEWÓDZTWO DOLNOŚLĄSKIE)

Zakład Hydrobiologii i Akwakultury
Uniwersytet Przyrodniczy we Wrocławiu

Abstrakt: Badania prowadzono na rzece Bystrzycy i jej dopływach. W pobranych próbkach wody oznaczono zawartość chromu(VI). Zawartość chromu w badanych wodach utrzymuje się na poziomie charakterystycznym dla wód powierzchniowych obszaru Polski o średnim stopniu zanieczyszczenia chromem. Lokalnie notowane podwyższenia stężeń są najprawdopodobniej wynikiem miejscowych zrzutów ścieków komunalnych i pochodzących z niewielkich zakładów przemysłowych.

Słowa kluczowe: chrom, woda rzeczna

DOI: 10.2428/ecea.2012.19(04)046 ECOL CHEM ENG A. 2012;19(4-5):441-449

Iwona ZYCH-WĘŻYK[1*] and Anna KRZEPIŁKO[1]

DETERMINATION OF TOTAL PHENOLIC COMPOUND CONTENT AND ANTIOXIDANT PROPERTIES OF EDIBLE BUCKWHEAT SPROUTS

POMIAR CAŁKOWITEJ ZAWARTOŚCI ZWIĄZKÓW FENOLOWYCH ORAZ WŁAŚCIWOŚCI ANTYOKSYDACYJNYCH JADALNYCH KIEŁKÓW GRYKI

Abstract: Consumption of buckwheat sprouts is strongly recommended because they have greater nutritional value than buckwheat seeds or products made from them. Sprouts are an excellent source of protein, amino acids, minerals, fibre, rutin and vitamins. Moreover, consumption of buckwheat sprouts is particularly recommended due to their high antioxidant activity and phenolic compound content. The aim of this study was to visually evaluate buckwheat sprouts based on differences in their morphological traits, to measure their total phenolic compound content and to determine total antioxidant capacity. Buckwheat seeds were moistened with distilled water and germinated in Petri dishes lined with filter paper in natural light conditions at 22 ^{o}C. Sprouts were collected on days 2–6 of the culture. Ethanol extracts were prepared from the sprouts. Total phenolic compound content was determined by spectrophotometry using Folin-Ciocalteau reagent as described by Pasko et al. Phenolic compound content was expressed in μM of gallic acid per 1 g of fresh mass. Three spectrophotometric methods were used to measure the total antioxidant capacity of buckwheat seedling extracts – the method described by Brand-Williams et al based on properties of DPPH, a method using the ABTS radical cation, and the FRAP method. Antioxidant content was expressed in μM of trolox per gram of fresh weight. Buckwheat sprouts were found to exhibit substantial antioxidant activity. The study showed that buckwheat sprouts are most suitable for eating on the fifth day of growth, when they have the best properties for consumption and the mean length of the seedling, measured from the root to the cotyledon, is 131.90 mm. The total phenolic compound content in the ethanol extracts of the buckwheat sprouts is highest on the third day – 3.40 μM of gallic acid per gram fresh weight. Antioxidant content measured by the various methods first increases, and then after the third day decreases slightly. The maximum TEAC per gram fresh weight was obtained on the third day: 73.56 μM of trolox with the ABTS method, 11.47 μM of trolox with the DPPH method and 128.99 μM of trolox with the FRAP method.

Keywords: buckwheat sprouts, total phenolic compound content, DPPH, ABTS, FRAP

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Introduction

Buckwheat belongs to the *Polygonaceae* family and is included among the "pseudocereals", i.e. plants which are not cereals but produce seeds rich in starch. The most popular species for cultivation are *Fagopyrum esculentum* Moench (grown in Poland, among other countries) and *Fagopyrum tartaricum* [1]. There has been increasing interest in buckwheat due to its health-promoting properties, including antineoplastic, antioxidant and antibacterial properties. Buckwheat is considered to be both an edible and a medicinal plant [2]. Rutin, which is used in the pharmaceutical industry, is obtained from its leaves and flowers. Rutin strengthens the capillaries of the circulatory system and has anti-inflammatory properties. Buckwheat is also used to produce vinegar, wine and tea [3]. Buckwheat grain does not contain gluten and is mainly processed for groats [1]. It is also used to produce flour from which pasta [4], bread and other products are produced. Buckwheat seeds are a good source of protein, containing more protein than rice or wheat [5]; moreover, they have high energy value and high content of unsaturated fatty acids (due to which antisclerotic activity is attributed to buckwheat) and are rich in microelements and vitamins. Buckwheat hulls obtained during production of groats are used to stuff pillows and mattresses [6]. Buckwheat is a valuable melliferous plant; buckwheat honey exhibits much higher antioxidant activity than acacia, linden, and multifloral honey, among others [7]. The main fatty acid in buckwheat seedlings is linoleic acid [8], while the main anthocyanin present in buckwheat sprouts is cyanidin 3-O-rutinoside (C3R) [9].

Buckwheat sprouts are an excellent source of protein, amino acids, minerals (Fe, Zn, Mn, Mg, Cu, Ca), fibre and rutin [2]. Moreover, the sprouts have higher nutritional value (more amino acids, minerals, protein, polyunsaturated fatty acids and crude fibres) than the seeds or seed products [10].

S.L. Kim et al demonstrated that the total amino acid content in buckwheat sprouts is about 28–38 % higher than in the seeds. Their research showed that buckwheat sprouts contain significantly more of such amino acids as aspartic acid, glutamic acid and lysine; however, the concentration of arginine and cysteine (amino acids containing sulphur) is lower than in the seeds [2].

This study presents results concerning the morphology and antioxidant content of edible buckwheat sprouts. Sprouts are a natural source of nutrients, fibre, vitamins and microelements. They contain significantly more concentrated nutrients than seeds and adults plants. During germination, high-molecular-weight reserve substances present in the seeds (proteins, carbohydrates and fats) are broken down into simple compounds that are easily assimilated by the human body. Furthermore, enzymes taking part in the breakdown of these substances facilitate the digestion of foods eaten with sprouts. Eating sprouts activates the immune system, corrects vitamin and mineral deficiencies, protects against many serious illnesses, and has antineoplastic effects.

The aim of the present study was to evaluate the morphology of buckwheat sprouts and to measure the total phenolic compound content and total antioxidant activity in ethanol extracts from buckwheat seedlings. Total phenolic compound content was determined by the method described by Singleton and Samuel-Raventos [11] and Pasko et al [12] using the Folin-Ciocalteu reagent. Three spectrophotometric methods were used to measure antioxidant activity in the seedling extracts: the method of Brand-Williams et al using the synthetic DPPH radical [13], the method using the ABTS radical cation described by Re et al, modified by Bartosz [14, 15], and the FRAP method proposed by Benzie et al in 1996 [16]. Spectrometric measurements were recorded using a Helios Epsilon VIS apparatus. The results will make it possible to choose the optimal time for consumption of buckwheat sprouts.

Materials and methods

Materials

Chemicals

2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), 1,1-diphenyl-2-picrylhydrazyl (DPPH), Folin-Ciocalteu reagent and 2,4,6-tris(2-pyridylo)-1,3,5-triazyne (TPTZ) were purchased from Sigma; trolox from Aldrich; potassium persulfate ($K_2S_2O_8$) from Sigma-Aldrich; ethanol, HCl, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ from POCH. All chemicals and reagents were analytical grade or purest quality.

Plant material

Buckwheat seeds for the study were purchased from Dary Natury. The seeds were moistened with distilled water and germinated on Petri dishes lined with filter paper at 22 ^{o}C in natural light conditions [17]. The seeds were watered. One gram of seedlings without seed coats was collected each day from days 2 to 6 after sowing. The seedlings were homogenized with 10 cm^3 of ethanol and the homogenate was centrifuged. The extracts were frozen and stored for further testing.

Methods

Examination of the morphology of the germinating buckwheat seeds

The morphological characteristics determined in the buckwheat seedlings were length of the entire seedling, number of seedlings per gram fresh weight, and the mass of one seedling. Seedling length was measured with a ruler and the results were given in millimetres. The mass of the seedlings was measured on an analytical balance and expressed in grams. The results of the direct measurements were analysed statistically.

Determination of total phenolics compound content

The total content of phenolic compounds was determined by the spectrophotometric method using the Folin-Ciocalteu reagent, described by Singleton and Samuel-Raventos [11] and Pasko et al [12]. This method is based on the reduction properties of phenolic compounds and involves measuring the absorbance of the complex resulting from the reaction of phenolic compounds with the Folin-Ciocalteu reagent. 0.3 cm^3 7 % Na_2CO_3, 0.15 cm^3 of Folin-Ciocalteu reagent and 2.9 cm^3 of water were added to 0.1 cm^3 of seedling extract. The absorbance of the reaction mixture was measured after 1 hour at a wavelength of 725 nm. Phenolic compound content was expressed as μM of gallus acid per 1 g fresh weight of seedlings.

Determination of DPPH radical scavenging activity

The antioxidant activity of the ethanol extracts from the seedlings was determined by the method using the synthetic radical DPPH (1,1-diphenyl-2-picrylhydrazyl). 50 mm^3 of the ethanol extract diluted 5-fold was added to 1500 mm^3 of an ethanol solution of DPPH. When DPPH reacts with an antioxidant, the stable DPPH radical takes on electrons from the antioxidant and loses its intense violet colour. The decrease in absorbance was measured in relation to the control sample (DPPH solution + ethanol) 30 minutes after the reaction was initiated, at a wavelength of 517 nm [13]. Antioxidant content was expressed as μM of trolox per 1 g fresh weight.

Determination of ABTS radical scavenging activity

The ABTS method for determining antioxidant activity is based on the reaction of the ABTS radical cation with antioxidants present in the extract, which is accompanied by a decrease in the intensity of the colour of the solution. A solution of ABTS radical cation produced beforehand by potassium persulfate oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) ammonium salt was added to 50 mm^3 of ethanol extract from the buckwheat seedlings, diluted 15-fold. Absorbance was measured 30 minutes after the reaction was initiated, at $\lambda = 414$ nm [14]. Antioxidant content was expressed as μM of trolox per 1 g fresh weight.

Determination of FRAP activity

In the FRAP method, the antioxidants contained in the extract reduce Fe^{3+}-TPTZ (*2,4,6-trypiridyl-s-trizine*) complex to Fe^{2+} ions. 1.500 mm^3 of a reaction mixture consisting of 10 mM TPTZ in 40 mM HCl, 20 mM $FeCl_3 \cdot 6H_2O$ and acetate buffer with pH 3.6, mixed in proportions of 1:1:10 (the FRAP reagent), heated to 37 ^oC, was added to 50 mm^3 of ethanol extract from the buckwheat seedlings, diluted 15-fold. Absorbance was measured after 15 minutes of incubation at 37 ^oC at a wavelength of 593 nm. A standard curve was prepared for $FeSO_4 \cdot 7H_2O$ [18]. The results were expressed in μM of iron ions reduced by the antioxidants contained in 1g fresh weight of seedlings.

All determinations were made in at least three independent replications.

Results and discussion

Buckwheat sprouts have a mild flavour and are slightly crunchy. They can be eaten as a fresh vegetable or in salads, or used for many other purposes, *eg* as material for producing natural vegetable juice [2]. Buckwheat sprouts grow rapidly; a root with a well-developed root-hair zone was observed on the second day of growth, and a shoot with well-developed cotyledons on the third day. Buckwheat sprouts attain a considerable size (Fig. 1); their average length is 49.83 mm on the third day of growth, and 161.27 mm by the sixth day. The average mass of one seedling also increases rapidly – 2.5 times between days 2 and 6 of growth (Fig. 2). The number of seedlings per 1g fresh weight decreases with the time of growth: 26.2 on the second day and 10.3 on the sixth. Buckwheat sprouts are best when eaten on days 4 and 5. It should be emphasized, however, that the root of the seedling grows very rapidly and on the sixth day accounts for about 3/4 of the length of the seedling. The edible part with better flavour is the shoot, and the root should be removed from seedlings over 6 days old.

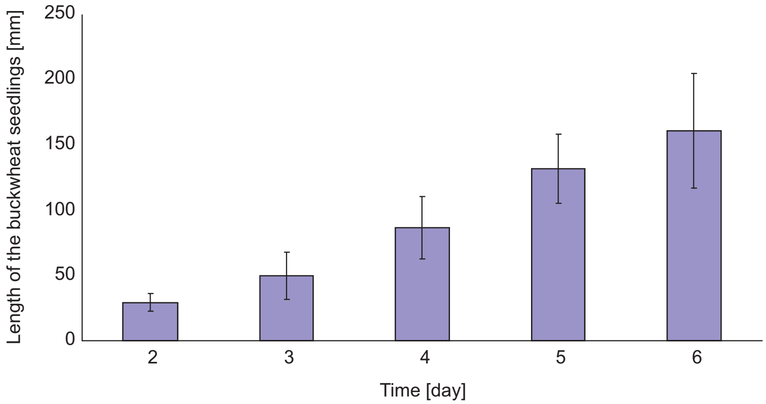

Fig. 1. Length of the buckwheat seedlings

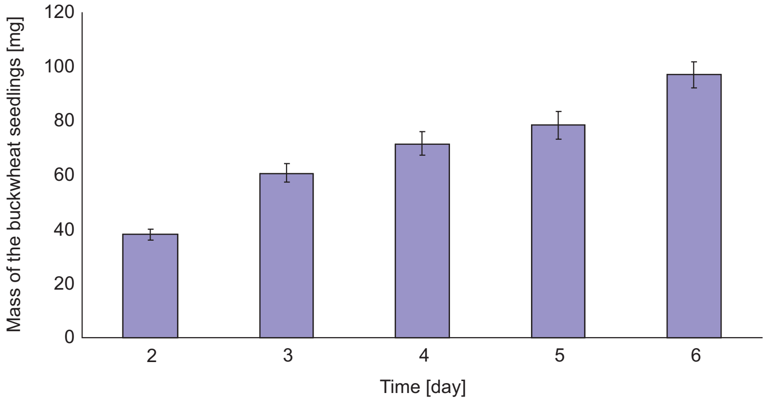

Fig. 2. Mass of the buckwheat seedlings

Determination of total antioxidant capacity and total phenolic compound content was begun after the second day of growth, when the sprouts had produced a radicle and most of them had an hypocotyl. Ethanol was used for the extracts due to the high content of phenolic compounds, particularly rutin. These compounds dissolve well in ethanol but very poorly in water [19].

Xu and Chang conducted a comparative study on the influence of the type of solvent on the phenolic compound content and antioxidant properties of a solution. The choice of solvent for the extraction depends on the type of substance being isolated, and different kinds of food require different kinds of solvents. When we use different solvents, we obtain different compositions of phenolic compounds and other antioxidants following extraction [20].

Phenolic compound content in the buckwheat seedlings ranged from 2.38 to 3.40 μM per gram fresh weight (Fig. 3). It was highest on the third day of growth, at 3.40 μM per gram fresh weight, and then the concentration decreased; on day 6 it was 2.38 μM per gram fresh weight, which is 85.3 % of the value for the 2-day-old seedlings. Buckwheat is very rich in phenolic compounds, which has been confirmed by other authors [21, 22]. The health-promoting effects of buckwheat in the human body are mainly due to its high rutin content. Rutin concentration in buckwheat depends on the organ of the plant and on the stage of development. S.L. Kim et al demonstrated that rutin concentration in buckwheat sprouts was 27 times higher than in the seeds; moreover, it increased each day after sowing. The authors showed that rutin concentration was highest on day 7, at 2933.7 mg/100 g DB [2]. Furthermore, Sharma et al noted the presence in buckwheat seedlings of such phenolic compounds as vitexin, isovitexin, orientin, isoorientin, quercetin and chlorogenic acid [22]. The amount of these phenolic compounds depends on the variety of buckwheat. The authors showed that rutin content is significantly higher in tartary buckwheat sprouts than in common buckwheat. Tartary buckwheat sprouts also contain more quercetin and chlorogenic acid.

Koyama et al found that the concentration and composition of phenolic compounds, particularly rutin, changes during germination of buckwheat; this observation has also been confirmed in the case of other plants: lupins [23] and lentils [24].

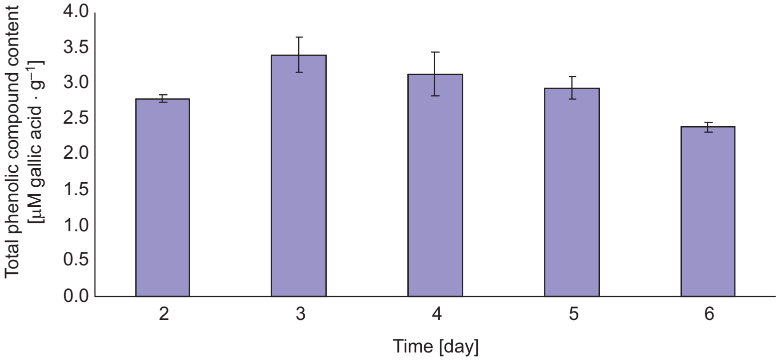

Fig. 3. Total content of phenolic compounds in the buckwheat seedlings

In lentils germinating in light, the concentration of trans-*p*-coumaric acid and trans-ferulic acid increases [24].

In the present study, three spectrophotometric methods were used to determine the antioxidant properties of the extracts. Each of these methods uses a coloured indicator substance: ABTS radical cation, DPPH radical or Fe^{3+}-TPTZ complex. When these substances react with the antioxidants contained in the sample, they lose their colour and the decrease in absorbance is proportional to the content of antioxidant compounds.

Total antioxidant capacity, as measured using the various methods, first increases and then begins to decrease slightly after the third day (Fig. 4). The maximum TEAC per gram of fresh weight was obtained on the third day of growth – 73.56 μM of trolox in the ABTS method, 11.47 μM of trolox in the DPPH method and 128.99 μM of trolox in the FRAP method. Due to the specificity of the reactions between the indicator substances and the antioxidants, different numerical values are obtained in the assays. If TEAC on the second day is given a value of 100 %, then on the third day the antioxidant content increases to about 125 % of the initial value in the ABTS method, 123 % in the DPPH method and 146 % in the FRAP method. On the sixth day, total antioxidant content decreases to about 88 % of the initial value in the ABTS method, 86 % in the DPPH method and 86.3 % in the FRAP method.

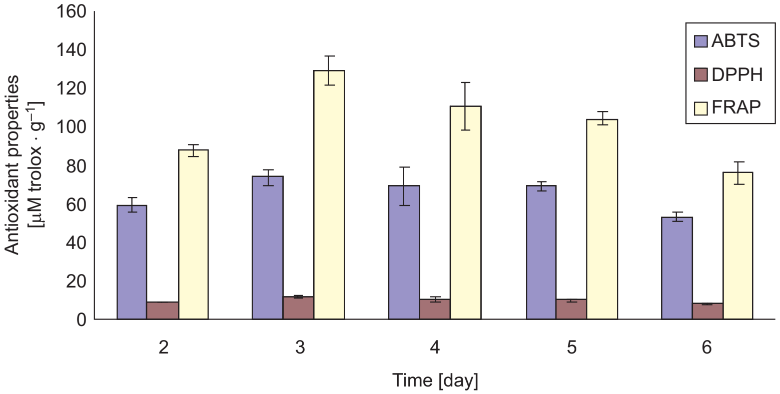

Fig. 4. Total antioxidant capacity of the buckwheat seedling extracts

Barton et al compared the results of measurements of antioxidant capacity obtained using different methods. According to the authors, the faster the reaction of the indicator substance, the higher the numerical values. They obtained the highest values using the FRAP method, intermediate values with the ABTS method, and the lowest values with the DPPH method [18].

A high correlation coefficient was noted between the results obtained using the three methods used to measure TEAC. The results also indicate a substantial correlation between the total phenolic compound content and the total antioxidant capacity of the extracts (Table 1), which may suggest that these compounds affect the antioxidant properties of sprouts. Other authors have also confirmed that the antioxidant properties of plant extracts are positively correlated with their phenolic compound content [20].

Table 1

Correlation coefficient between TEAC as determined by the methods used and the total content of phenolic compounds

	DPPH	FRAP	Total phenolic compound content
ABTS	0.9322	0.9604	0.9496
DPPH		0.9845	0.9947
FRAP			0.9813

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POMIAR CAŁKOWITEJ ZAWARTOŚCI ZWIĄZKÓW FENOLOWYCH ORAZ WŁAŚCIWOŚCI ANTYOKSYDACYJNYCH JADALNYCH KIEŁKÓW GRYKI

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Abstrakt: Spożywanie kiełków gryki jest szczególnie polecane, gdyż wykazują lepszą wartość odżywczą niż nasiona gryki czy produkty z nich powstałe. Kiełki są doskonałym źródłem białka, aminokwasów, minerałów, błonnika, rutyny oraz witamin. Ponadto spożywanie kiełków gryki jest polecane ze względu na ich znaczną aktywność antyoksydacyjną oraz zawartość związków fenolowych. Celem prezentowanej pracy była ocena wizualna kiełków gryki na podstawie różnic w cechach morfologicznych, pomiar całkowitej zawartości związków fenolowych oraz pomiar całkowitej zdolności antyoksydacyjnej.

Nasiona gryki zwilżone wodą destylowaną kiełkowały na szalkach Petriego wyłożonych bibułą filtracyjną, w naturalnych warunkach oświetlenia, w temperaturze 22 ^{o}C. Kiełki gryki zbierano od 2 do 6 dnia hodowli. Przygotowano etanolowe ekstrakty z siewek. Całkowitą zawartość związków fenolowych oznaczano metodą spektrofotometryczną z wykorzystaniem odczynnika Folina-Ciocalteau opisaną przez Paśko i współpr. Zawartość związków fenolowych wyrażono w μM kwas galusowego w przeliczeniu na 1 g świeżej masy. Do pomiaru całkowitej zdolności antyoksydacyjnej ekstraktów z siewek zastosowano metodę Brand-Wiliams i współpr. wykorzystującą właściwości DPPH, metodę ABTS oraz metodę FRAP. Zawartość antyoksydantów wyrażano w μM troloxu na 1 gram świeżej masy. Kiełki gryki wykazują znaczną aktywność antyoksydacyjną. Z przeprowadzonych badań wynika, że piąty dzień hodowli jest najbardziej odpowiednim dniem do spożycia tych kiełków. Kiełki mają w tym dniu najlepsze właściwości konsumpcyjne a średnia długość siewki mierzona od korzenia do liścieni wynosi 131.90 mm. Całkowita zawartość związków fenolowych w etanolowych ekstraktach z kiełków gryki jest w trzecim dniu największa i wynosi 3.40 μM kwasu galusowego w przeliczeniu na gram świeżej masy. Zawartość antyoksydantów mierzona różnymi metodami początkowo rośnie a po trzecim dniu hodowli nieznacznie spada. W trzecim dniu hodowli uzyskano maksymalna wartość w przeliczeniu na świeżą masę, wynosiła ona 73.56 μM troloxu w metodzie ABTS, 11.47 μM troloxu w metodzie DPPH i 128.99 μM troloxu w metodzie FRAP.

Słowa kluczowe: kiełki gryki, całkowita zawartość związków fenolowych, DPPH, ABTS, FRAP

DOI: 10.2428/ecea.2012.19(04)047 ECOL CHEM ENG A. 2012;19(4-5):451-456

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DETERMINATION OF BENZOIC AND SORBIC ACIDS IN FOODS

OZNACZANIE ZAWARTOŚCI KWASU BENZOESOWEGO I SORBOWEGO W PRODUKTACH SPOŻYWCZYCH

Abstract: The aim of this work was the analysis of benzoic acid and sorbic acid content in selected beverages and processed fruit and vegetable products. The analyses of these preservatives in 34 different food products (ketchups, carbonated and non-carbonated beverages, beverage concentrates) were performed. In this purpose, the conditions of analyzed compounds extraction from the food samples were optimized and method of analysis by reversed-phase high performance liquid chromatography method (RP-HPLC) was developed. Very good separation of the analytes was achieved using methanol-water-acetate buffer pH 4.4 (40 : 40 : 20) as a mobile phase.

Keywords: food preservatives, benzoic acid, benzoates, sorbic acid, sorbates, beverages, fruit and vegetable products

Majority of food products available on the market contain different types of additives, among which preservatives are playing an important role. These additives, applied in order to maintain food quality and prolong storage time, often make consumers anxious about its safety. Very popular preservatives are benzoic acid and sorbic acid, used mostly in the form of the well soluble sodium, potassium or calcium salts. These compounds retard the growth of yeast and moulds and are effective against wide range of bacteria [1]. Analytical methods used for their determination are based mainly on UV spectrophotometry, *gas chromatography* (GC) and *high performance liquid chromatography* (HPLC) [2–6]. These preservatives very often are used together due to its complementary properties, so the simultaneous determination of these two acids is desirable. In many cases prior to the analysis sample preparation is required, in order to isolate the analytes from the complex food samples. The aim of this work was the analysis of benzoic and sorbic acid content in selected beverages and processed fruit and vegetable products. In this purpose, the conditions of analyzed compounds extraction from the food samples were optimized and method of analysis by *reversed-phase high performance liquid chromatography* method (RP-HPLC) was developed.

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Materials and methods

The analyses of benzoic and sorbic acid used as the preservatives in different food products available on the home market (ketchups, carbonated and non-carbonated beverages, beverage concentrates) were performed.

Analytes were extracted from the food samples by chloroform after previous salting out using natrium chloride solution. In order to optimize this step, the influence of different factors during sample preparation was studied (solvent volume, multiplication, pH, filtration). It was found that using chloroform as a extraction solvent, more than 95 % of analytes were obtained in the first three extractions; in the samples from fifth extraction analytes were not found. So it was stated that four extractions with 5 cm^3 of chloroform is proper. The time consumable filtration process of salted out sample which was used in preliminary works appeared to be not necessary. Instead of this centrifugation of final sample was performed.

Finally, 2.5 g of ketchup or 15 cm^3 of beverage was placed in a measuring flask, filled to 25 cm^3 volume with saturated natrium chloride solution and well mixed. Carbonated beverages were degassed previously by using water aspirator. Next, 20 cm^3 of obtained solution was placed in separatory funnel and extracted four times by using 5 cm^3 of chloroform. All extracts were connected and filled up to 25 cm^3 volume with methanol. Before the chromatographic analysis samples were centrifuged.

The analyses were performed by *high performance liquid chromatography* (HPLC) method. The reversed phase mode was applied, with *non-polar octadecylsilane* (C18) stationary phase and polar mobile phase with lowered pH. LC-5B liquid chromatograph equipped with UV-VIS detector and glass column (150 × 3.3 mm I.D.) filled with SEPARON SGX C-18 (7 μm) stationary phase was used. The monitoring wavelength was $\lambda = 254$ nm. The analyses were performed at room temperature with the mobile phase flow rate 0.5 cm^3/min.

The composition of eluent was optimized in order to achieve good separation of benzoic acid, sorbic acid and chloroform. In this purpose, different mobile phases were prepared using mixtures of methanol and water, with pH lowered by addition of acids or buffer. Due to the similarity of pK_a values of benzoic and sorbic acid (4.21 and 4.76, respectively) separation by reversed phase liquid chromatography is difficult. Using mobile phases with additions of acids, with pH 3.0 (0.1 % of phosphoric acid) or 3.6 (1 % of acetic acid), separation of analytes was not achieved. Good separation was enabled by using eluents of pH between pK_a values of analytes (with addition of acetic buffer pH 4.4). For all tested mobile phases, retention times of benzoic and sorbic acid and extraction solvent (chloroform) was measured and peak resolution (R_s) was calculated from the formula [7]:

$$R_s = 1.177\ d\ /\ (w_{0.5(1)} + w_{0.5(2)})$$

where: d – distance between peaks centers [mm],
$w_{0.5}$ – widths at half height of peaks [mm].

Among the tested eluents the best results provided mixture of methanol (40 %), water (40 %) and acetic buffer pH 4.4 (20 %) and it was finally used as a mobile phase. For this eluent the obtained value of R_s factor for benzoic and sorbic acid was high above minimum criteria value 1.5 (complete resolution to the baseline) and the time of analysis was much shorter than using mobile phase with 30 % of methanol. The obtained data are presented in Table 1.

Table 1

Retention times and peak resolutions of benzoic and sorbic acids obtained for different mobile phase compositions

Mobile phase composition	Retention time [min]			Peak resolution R_s
	Benzoic acid	Sorbic acid	Chloroform	
50 % methanol 49.9 % water 0.1 % phosphoric acid	4.83	4.83	6.18	0
50 % methanol 49 % water 1 % acetic acid	5.30	5.30	6.25	0
50 % methanol 30 % water 20 % acetic buffer (pH 4.4)	3.67	4.17	6.25	1.36
40 % methanol **40 % water** **20 % acetic buffer (pH 4.4)**	**5.28**	**6.75**	**10.35**	**2.97**
30 % methanol 50 % water 20 % acetic buffer (pH 4.4)	8.37	11.33	16.67	3.52

Identification of preservatives in various foodstuffs was based on the retention time comparison of peaks obtained in analysis of the standard solutions and the samples. Quantification was performed by external standard method using calibration curves which were rectilinear in the range of method application (correlation coefficients: 0.9980 for benzoic acid and 0.9997 for sorbic acid). *The limits of detection* (LOD) were determined by decreasing the concentration of the prepared standard solutions to achieve the smallest detectable peaks, and multiplying these concentrations by 3. The estimated LOD values in proposed method were 4.0 mg/dm^3 for benzoic acid and 0.12 mg/dm^3 for sorbic acid. These values are much below the permitted limits detailed for the individual foods, which are in majority of cases between 150 mg/dm^3 – 1000 mg/dm^3 or mg/kg for benzoic acid and 200 mg/dm^3 – 2000 mg/dm^3 or mg/kg for sorbic acid [8].

Results and discussion

The performed analyses of 9 different types of *ketchups* (K) confirmed that in agreement with the producer's information, in two of them preservatives were not detectable. In the remaining 7 ketchups sodium salt of benzoic acid was applied. The level of benzoic acid in one of them (1776 mg/kg) was found to be high above the maximum allowed limit for this group of products (1000 mg/kg). The content of benzoic acid in other samples ranged from 226 mg/kg to 1009 mg/kg (Table 2).

Table 2

Preservatives contents in *ketchups* (K)

Product	Benzoic acid [mg/kg]	Sorbic acid [mg/kg]	Summary content (benzoic + sorbic acid) [mg/kg]
K-1	416	n.d.	416
K-2	941	n.d.	941
K-3	226	n.d.	226
K-4	1776	n.d.	1776
K-5	660	n.d.	660
K-6	1009	n.d.	1009
K-7	695	n.d.	695
K-8	n.d.	n.d.	n.d.
K-9	n.d.	n.d.	n.d.

n.d. – not detected.

The results of the analyses of the *non-carbonated* (NCB) and *carbonated beverages* (CB) are collected in Tables 3 and 4, respectively. All analyzed non-carbonated beverages contained benzoic acid in the range of 73 mg/dm^3 – 174 mg/dm^3, and additionally in two samples sorbic acid (27 mg/dm^3 and 30 mg/dm^3) was found. Majority of the analysed carbonated beverages contained benzoic acid (16–406 mg/dm^3) or its mixture with sorbic acid (73–169 mg/dm^3), in one sample only sorbic acid was applied (169 mg/dm^3). The amount of benzoic acid in two samples was above the maximum allowed limit for beverages – 150 mg/dm^3. The limit for sorbic acid in beverages was set at 300 mg/dm^3 when it is used separately or 250 mg/dm^3 when it is applied together with benzoic acid. These values were not exceeded in none of the analysed samples of beverages.

Table 3

Preservatives contents in *non-carbonated beverages* (NCB)

Product	Benzoic acid [mg/dm^3]	Sorbic acid [mg/dm^3]	Summary content (benzoic + sorbic acid) [mg/dm^3]
NCB-1	142	n.d.	142
NCB-2	73	27	100
NCB-3	73	30	103
NCB-4	141	n.d.	141
NCB-5	128	n.d.	128
NCB-6	174	n.d.	174
NCB-7	132	n.d.	132

n.d. – not detected.

Table 4

Preservatives contents in *carbonated beverages* (CB)

Product	Benzoic acid [mg/dm^3]	Sorbic acid [mg/dm^3]	Summary content (benzoic + sorbic acid) [mg/dm^3]
CB-1	149	84	233
CB-2	133	73	206
CB-3	136	n.d.	136
CB-4	92	n.d.	92
CB-5	117	n.d.	117
CB-6	138	n.d.	138
CB-7	78	n.d.	78
CB-8	132	n.d.	132
CB-9	123	n.d.	123
CB-10	129	n.d.	129
CB-11	n.d.	169	169
CB-12	93	88	181
CB-13	16	169	185
CB-14	406	n.d.	406

n.d. – not detected.

The analyses of selected *beverage concentrates* (BC) showed that calculated summary content of benzoic and sorbic acid in these products (after dilution according to the producer's recommendation) ranges between 76 mg/dm^3 and 189 mg/dm^3. These values, collected in Table 5, are below the maximum summary content limit of these two acids – 600 mg/dm^3.

Table 5

Preservatives contents in *beverage concentrates* (BC)

Product	Benzoic acid [mg/dm^3]	Sorbic acid [mg/dm^3]	Summary content (benzoic + sorbic acid) [mg/dm^3]	Recommended dilution of product (v:v)	Summary content (benzoic + sorbic acid) in diluted product [mg/dm^3]
BC-1	919	n.d.	919	1:10	92
BC-2	857	n.d.	857	1:10	86
BC-3	n.d.	304	304	1:4	76
BC-4	166	588	754	1:4	189

n.d. – not detected.

The obtained data indicate that the preservatives content in foods exceeded the permitted maximum levels only accidentally.

Conclusions

The analyses of benzoic and sorbic acid content in 34 different food products (ketchups, carbonated and non-carbonated beverages, beverage concentrates) were performed by high performance liquid chromatography. The proposed method enables the simultaneous and selective analysis of these popular preservatives in different types of products.

On the basis of the obtained results it was found that the content of the analyzed preservatives in most cases was below the permitted level. In one ketchup sample and two beverages samples, amount of benzoic acid significantly exceeded the allowed values.

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OZNACZANIE ZAWARTOŚCI KWASU BENZOESOWEGO I SORBOWEGO W PRODUKTACH SPOŻYWCZYCH

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Abstrakt: Przedmiotem badań była analiza zawartości kwasu benzoesowego oraz kwasu sorbowego w wybranych napojach i produktach owocowo-warzywnych. Oznaczono zawartość tych konserwantów w 34 artykułach żywnościowych: ketchupach, napojach gazowanych i niegazowanych oraz zaprawach do napojów. W tym celu dobrano warunki ekstrakcji oznaczanych związków z próbek artykułów spożywczych oraz opracowano metodę ich analizy za pomocą *wysokosprawnej chromatografii cieczowej w odwróconym układzie faz* (RP-HPLC). Bardzo dobry rozdział analitów uzyskano przy zastosowaniu jako fazy ruchomej mieszaniny metanol–woda–bufor octanowy pH 4,4 (40 : 40 : 20).

Słowa kluczowe: konserwanty, kwas benzoesowy, benzoesany, kwas sorbowy, sorbiniany, napoje, produkty owocowo-warzywne

DOI: 10.2428/ecea.2012.19(04)048 ECOL CHEM ENG A. 2012;19(4-5):457-470

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MODELING OF ULTRAFILTRATION PROCESS EFFICIENCY IN COKE PLANT WASTEWATER TREATMENT WITH THE USE OF INDUSTRIAL MEMBRANES

MODELOWANIE WYDAJNOŚCI PROCESU ULTRAFILTRACYJNEGO OCZYSZCZANIA ŚCIEKÓW KOKSOWNICZYCH Z ZASTOSOWANIEM MEMBRAN KOMERCYJNYCH

Abstract: In the research conducted there was determined the coke plant waste treatment efficiency in the integrated process that combines ultrafiltration with the reverse osmosis system. In both pressure filtration methods commercial Osmonics membranes were applied. The degree of removal efficiency was evaluated according to changes in the values of selected pollution indicators that characterized “raw” and cleaned wastewater. On the basis of the relaxation method assumptions there was made an attempt to predict the efficiency of the membranes used at the initial stage of ultrafiltration process carried out in non-stationary arrangement. The values of the initial permeate flux and saturation flux, experimentally determined, as well as time constants, determined graphically, allowed to calculate theoretical temporary permeate flux for selected low pressure membranes.

Keywords: ultrafiltration, coke plant wastewater, high pressure membrane techniques, commercial membranes, mathematical model

Introduction

Great diversification of toxic substances found in coke-plant waste, such as polycyclic aromatic hydrocarbons, heterocyclic compounds, oils, tars, cyanides, sulfides, sulfates, thiosulphates, ammonia, and heavy metals extort the application of integrated purification systems that combine single processes used in sewage treatment technology [1–2].

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New efficient methods are being searched in order to guarantee the required removal efficiency of wastewaters treatment that will allow to pour them into natural receivers or reuse them for technical purposes, such as coke quenching. One of them are pressure-driven membrane processes.

The application of those processes requires the reduction of fouling process, which is caused by the substances presented in cleaning waste (pore blocking effect). It restricts permeate volume flux and its declination velocity in the process of pressure filtration, and it decides of membrane usability.

In this work there has been made an attempt to define the possibility of predicting the polysulfone ultrafiltration membranes efficiency in the coke plant wastes treatment using ultrafiltration-reverse osmosis system. The experiment was carried out on the basis of relaxation model, which describes the permeate flux changes in the membrane filtration in the non-stationary arrangement [3–5].

Testing equipment

In the process of coke plant wastes membrane treatment there was used the apparatus unit equipped with a plate-frame membrane module of the type: SEPA CF-NP produced by an American company: Osmonics. It is equipped with: a container of 8 dm^3 capacity, rotameter, the high-pressure pump, manometers and valves. The module membrane worked in cross-flow system with return retentate. The installation applied in the research is presented in Fig. 1.

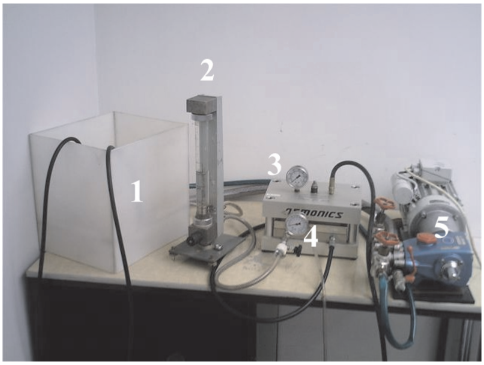

Fig. 1. Testing equipment for coke plant wastewater treatment: 1 – tank, 2 – rotameter, 3 – plate and frame module membrane, 4 – manometer, 5 – high pressure pump

Materials and methods

Raw wastewater

The treated coke plant wastes came from ISD Steelworks Czestochowa Coke Plant “Koksownia Częstochowa Nowa” Ltd. The sewage was initially treated mechanically where tars, oils and stable impurities were removed and then they were subject to the gas desorption in order to remove ammonia. Table 1 shows the values of the chosen pollution indexes which are characteristic for coke plant sewage after initial treatment stage.

Table 1

The characteristics of coke plant wastes coming from ISD Steelworks Czestochowa Coke Plant "Koksownia Częstochowa Nowa" Ltd. after initial treatment

Indicator	Unit	Value	The indexes of sewage pollution which is carried away to the receiver[1]	Technical water – to quenching of coke[2]
pH	—	8.70–10.9	6.50–9.00	—
COD	mgO_2/dm^3	6500–3100	125	—
BOD_5	mgO_2/dm^3	20–80	25.0	—
Volatile ammonia as NH_4^+	$mgNH_4^+/dm^3$	25.0–134	10.0	82.0
TC	mgC/dm^3	1184.6	n.s.	—
TOC	mgC/dm^3	963.1	30.0	—
Phenols	mg/dm^3	20.0–30.0	0.10	15.0
Cyanides	mg/dm^3	10.0–50.0	0.10	9.00
Conductivity	mS/cm	7.25–10.9	n.s.	—

TC – total carbon, TOC – total organic carbon, n.s. – not standardized.

[1] Regulation of the Minister of Environment dated 28 January 2009 amending the Regulation on of the conditions to be met for the introduction of sewage into the water or soil, and on substances particularly harmful to the aquatic environment (Journal of Laws No. 27 item 169).

[2] BAT – *Best Available Techniques* for coking plant, December 2005.

Membranes

In the research were applied 4 types of ultrafiltration polymer flat membranes (HZ15, PVDV, PW, DS-GM) and one reverse osmosis polymer membrane ADF. All the flat membranes were produced by the American Osmonics company from different polymers. Their characterization provided by the producer are shown in Tables 2 and 3.

Table 2

The characteristics of commercial ultrafiltration membranes applied in initial coke-making wastewater treatment [4]

Membrane	Polymer	Indicator	Cut-off	pH	J_V/psi	Pressure [bar]	Cl [ppm]	Temperature [°C]
UF	PS	HZ15	20K	0.5–13	85/30	1.7	5000	80
UF	PES	PW	10–12K	2–11	85/30	2	5000	90
UF	TF	DS-GM	8K	2–11	275/30	14	5000	90
UF	PVDV	PVDV	30K	1–11	275/30	2	5000	90

Table 3

The characteristics of commercial reverse osmosis membrane applied in coke-making wastewater treatment [4]

Membrane	Polymer	Indicator	Retention coefficient [%]	pH	J_V/psi	Pressure [bar]	Cl [ppm]	Temperature [°C]
RO	polyamide (AD)	ADF	99.5	4–11	15/800	54	1000	50

Analytical methods

At the first stage of the experiment the membranes were subjected to conditioning process which allowed to form their structures in a stable way. This process consisted in the filtrating of deionized water through the membranes at the changeable trans-membrane pressure within the range of $0.2 \cdot 10^6$ Pa to $0.8 \cdot 10^6$ Pa and with the flow speed above the surface equal: 2.0 m/s. The membranes were conditioned up to the moment of stabilization of the size of deionized water flux within the time.

At the further stage of the experiment their transport properties were determined: the relation between volumetric flux of deionized water and the time of the low-pressure filtration process at the $0.4 \cdot 10^6$ Pa and with the flow speed above the surface equal: 2.0 m/s.

In the next stage of the research there was stated the usefulness of the membrane in coke plant wastewater preliminary treatment. The evaluation criteria were: changes of the values of the membrane hydraulic permeability and relative penetrability of the lead under low-pressure filtration and the degree of the load of impurities removal. The effectiveness of the process was evaluated on the basis of the impurities indexes changes which characterized crude and treated sewage. There was determined COD, TC, TOC and concentration of ammonium nitrogen, cyanides and phenols.

The COD indicators were obtained by means of the test method on the HACH DR 4000 spectrophotometer, while the determination of: TOC, and TC was achieved by means of high temperature catalytic oxidation method with the usage of a chromatograph. Concentration of ammonium nitrogen was determined by distillation directly method, phenols were determined by *p*-nitroaniline titration method and concentration of cyanides was determined by titration of barbituric acid.

The research results demonstrated, that the pollution indicators for the cleaned sewages for all types of membranes were too high in comparison with the standards. Therefore, they were treated additionally with the reverse osmosis method where the ADF Osmonics membrane was applied.

The degree of the removal efficiency was evaluated according to pollution indicators changes, as it was in the case of the low pressure filtration process.

At the last stage of the research there was made an attempt to define the possibility to predict commercial membranes efficiency in the coke plant wastewater treatment based on relaxation model assumptions, which shows the permeate stream changes in the membrane filtration carried out in nonstationary arrangement.

Results and discussion

The transport properties of the ultrafiltration polysulfone membranes

Transport properties of membranes were determined by précising the dependence of the flux of volumetric deionized water on the transmembrane pressure. The carried out measurements proved the significantly diversified dependence of the hydraulic membranes productivity on different structure density and polymers used (Fig. 2).

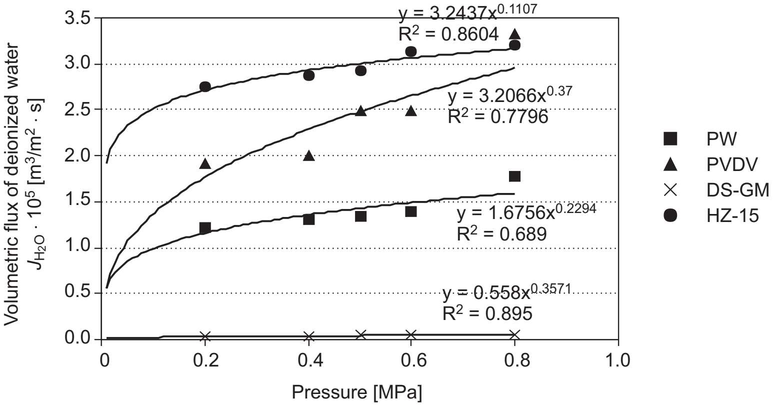

Fig. 2. Dependence of volumetric flux of deionized water on ultrafiltration membranes pressure

From all ultrafiltration membranes tested, the DS-GM membrane had the lowest volumetric flux ($J_{H_2O} = 0.037 \cdot 10^{-5}$ m^3/m^2 · s; $\Delta P = 0.4$ MPa), whereas the highest efficiency had the HZ-15 membrane ($J_{H_2O} = 2.865 \cdot 10^{-5}$ m^3/m^2 · s; $\Delta P = 0.4$ MPa). Indicated dependences $J_{H_2O} = f(\Delta P)$ were described by the means of exponential equations, and high values of correlation coefficient showed the right selection of regression line according to measurement results.

The selection of the most beneficial ultrafiltration membrane to the coke plant wastes pretreatment

Membrane efficiency, its relative penetrability, and degree of removal efficiency were the factors to determine which of the membranes were the most useful for the initial coke plant wastewater treatment. Figure 3 shows the dependence of the flow of purified wastewater flux on the low pressure filtration time.

It was stated that during the coke plant wastewater low pressure filtration DS-GM membrane had the lowest volumetric permeate flux. After 90 minutes of ultrafiltration process, the steady permeate flux had the value of $0.0289 \cdot 10^{-5}$ m^3/m^2 · s. However, the highest permeate stream had the HZ-15 membrane with the stream 22 times higher ($0.636 \cdot 10^{-5}$ m^3/m^2 · s). Figure 4 shows the comparison of relative permeability changes in the discussed process.

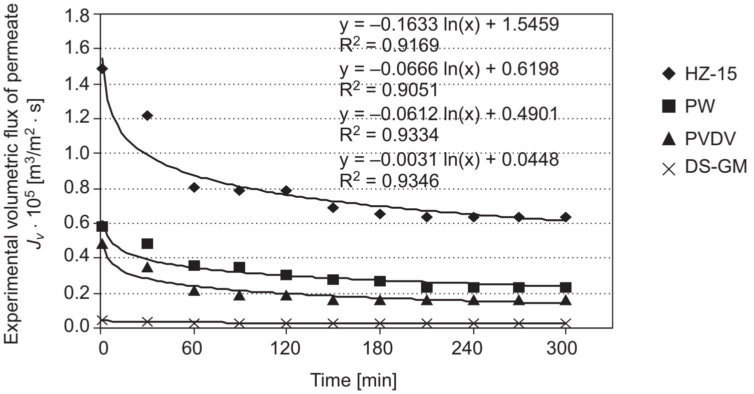

Fig. 3. Dependence of temporary experimental volumetric flux on time of coke-making ultrafiltration process for commercial membranes (ΔP = 0.4 MPa)

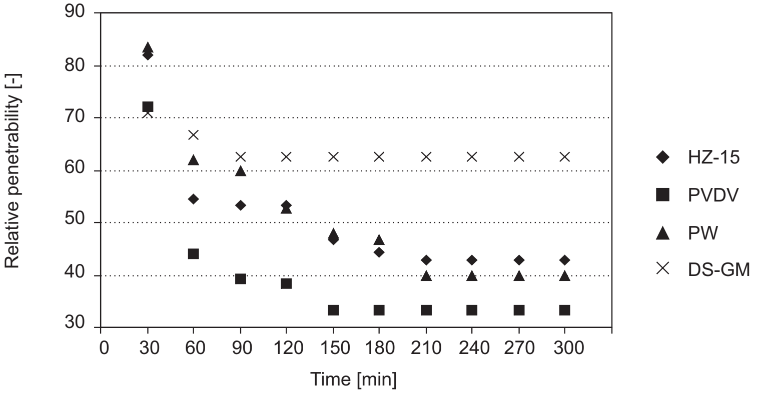

Fig. 4. Commercial membranes relative penetrability changes in relation with the time of coke-making ultrafiltration process

The relative penetrability of the membrane was defined as the quotient of the temporary experimental flux of permeate (J_v) to the stabilized flux of deionized water (for the same transmembrane pressure and of flow speed above the surface).

The highest relative permeability had DS-GM membrane, and the lowest PVDV membrane. Its permeability value was significantly lower.

The degree of wastewater purification was determined by the change of pollution indicators in "raw" and cleaned wastewater. Coke-plant wastewater were characterized by the following pollution indicators: COD – 4519.6 mgO$_2$/dm^3, TC – 1186.4 mgC/dm^3, TOC – 963.1 mgC/dm^3, and the concentration of phenols and cyanides consequently: 27.3 mg/dm^3 and 38.1 mg/dm^3 (Table 4).

The most advantageous was considered DS-GM industrial membrane. The pollution indicators rate in its case was the lowest.

Table 4

The stages of pollutions removal in coke-making wastewater ultrafiltration process with use of commercial membranes

Indicator	Unit	Raw wastewater	Cleaned wastewater							
			PVDV	Stage of removal of pollutions [%]	PW	Stage of removal of pollutions [%]	DS-GM	Stage of removal of pollutions [%]	HZ-15	Stage of removal of pollution [%]
COD	mgO_2/dm^3	4519.6	3755.9	16.9	3789	16.2	2707.6	40.1	4029.1	10.8
TC	mgC/dm^3	1186.4	590.8	50.2	698.6	41.1	451.7	62.0	855.4	27.9
TOC	mgC/dm^3	963.1	523.8	45.3	646.6	32.8	378.1	60.7	727.1	24.5
Volatile ammonia as NH_4^+	$mgNH_4^+/dm^3$	131.6	119	9.6	121.5	7.6	98.0	25.5	125	5.0
Cyanides	mg/dm^3	38.1	36.3	4.6	36.3	4.8	35.5	6.8	36.8	3.5
Phenols	mg/dm^3	27.3	24.9	8.8	24.6	9.7	24.2	11.4	25.1	8.0

TC – total carbon, TOC – total organic carbon.

Table 5

The efficiency of the coke plant wastewater treatment in the integrated ultrafiltration – reverse osmosis system

Indicator	Unit	Raw wastewater	Treated wastewater				Permissible standards	Technical water – to quenching of coke
			UF/DS-GM		RO/ADF			
			Unit	The degree of the impurities removal [%]	Unit	The degree of the impurities removal [%]		
COD	mgO_2/dm^3	4519.6	2711.7	40.1	109	97.6	125	—
TC	mgC/dm^3	1186.4	451.7	62.0	22.0	98.15	n.s.	—
TOC	mgC/dm^3	963.1	378.1	60.7	15.0	98.44	30.0	—
Volatile ammonia as NH_4^+	mg/dm^3	131.6	98.0	25.5	21.0	84.0	10.0	82.0
Cyanides	mg/dm^3	38.1	35.5	6.8	0	100	0.10	9.0
Phenols	mg/dm^3	27.3	24.2	11.4	0	100	0.10	15.0
Conductivity	mS/cm	8.41	7.9	—	0.89	—	—	—

TC – total carbon, TOC – total organic carbon., n.s. – not standardized.

Cleaned wastewater was characterized by the following pollution indicators: COD – 2711.7 mgO_2/dm^3, total carbon TC – 451.7 mgC/dm^3, total organic carbon TOC – 378.1 mgC/dm^3, and the concentration of phenols and cyanides consequently: 24.2 mg/dm^3 and 35.5 mg/dm^3.

However, all the values exceeded significantly the standards of quality that allow to pour cleaned wastewater into water container or drainage. It was also inadequate to reuse it as a medium for coke quenching. Taking this into consideration a decision of applying a reverse osmosis process was taken (Table 5).

The additional treatment of coke plant wastes after their initial treating were characterized by the following pollution indicators: COD – 109 mgO_2/dm^3, concentration of total organic carbon and total carbon consequently: 22 mgC/dm^3 and 15 mgC/dm^3, concentration of ammonium nitrogen in calculated as volatile ammonia as NH_4^+ was 21 mgNH_4^+/dm^3. In the permeate participation of cyanides and phenols was not stated.

The obtained results of research can lead to the conclusion that the sewage additionally treated in the process of reverse osmosis still did not meet the standards of quality given by the decree of Environment Minister from 28th January 2009. Concerning the conditions which should be fulfilled to pour away the sewage into water and to the soil and concerning the substances which are particularly harmful for water environment, the concentration of ammonium nitrogen was high. In the research the concentration of ammonium nitrogen calculated as volatile ammonia NH_4^+ was two times higher, before having been carried out by steam stripping process. Treated wastewater can be used as technical water for quenching of coke.

The modeling of the low-pressure filtration process in the process of treating the coke plant wastes

In this work there was made an attempt to define the possibility of predicting the polysulfone ultrafiltration membranes efficiency in the process of treating the coke plant wastes, based on relaxation model assumptions, which describes the permeate stream changes in the membrane filtration carried out in the non-stationary arrangement [3, 5–8]. There was mathematically determined the dependence of theoretical, temporary permeate flux on the time of the pressure filtration and then it was compared with the experimental flux. In the relaxation model the balance of mass transportation in the process of membrane filtration is presented by equation [5].

$$\frac{d}{dt}(J - J_\infty) + \frac{t}{t_0}(J - J_\infty) = 0 \tag{1}$$

At the assumptions that $J(t)_{t=0} = J_0$

That allows to determine the permeate flux changes in the process of filtration. The knowledge about the initial fluxes: initial (J_0), equilibrium – saturation (J_∞) and time constant (t_0) enables the solution of the following equation:

$$\ln\left(\frac{J - J_\infty}{J_0 - J_\infty}\right) = -\frac{t}{t_0} \tag{2}$$

where: $J_{t=0} = J_0$,
$J_{t\to\infty} = J_\infty$,
t_0 – time constant.

The time constant which characterizes the velocity of stream disappearing was determined from the equation (2) by means of graphic method:

$$t_0 = |\,1/a\,| \tag{3}$$

where: a – the straight line coefficient ($y = a \cdot t$) characterizes the filtration process for the examined membrane.

The formula conversion (2) allows to determine the relation between the theoretical, temporary, volumetric flux of permeate (J_t) and the time of the filtration process:

$$J_t(t) = (J_0 - J_\infty)\, e \frac{t}{t_0} + J_\infty \tag{4}$$

The theoretical average value of the permeate stream is determined by solving the equation (5):

$$J_a = \frac{1}{t_0}\int_0^{t_0} J_t(t)\,dt = J_0 - \frac{(J_0 - J_\infty)}{e} = J_0 - 0.37\,(J_0 - J_\infty) \tag{5}$$

within the integration limits: $t = 0$ and $t = t_0$.

Whereas experimental average value of flux was described by equation:

$$J_{ae} = \frac{1}{t_r}\int_0^{t_r} J_e(t)\,dt \tag{6}$$

where: t_r – time longer than: t_0 in which the volumetric permeate stream achieves the equilibrium value determined as J_∞.

In Table 6 there were compared experimentally the quantities which are characteristic for the ultrafiltration process of treating coke plants wastes on the selected ultrafiltration membranes, and graphic way of determining the time constant. Below on Figure 5 shows, however, the example of graphic way of determining the time constant: t_0 for the best DS-GM membrane.

Table 6

Properties of coke making wastewater ultrafiltration process characteristics

Membranes	$J_0 \cdot 10^{-5}$ [m^3/m$^2 \cdot$ s]	$J_\infty \cdot 10^{-5}$ [m^3/m$^2 \cdot$ s]	t_0 [min]
PW	0.578	0.231	250
PVDV	0.482	0.162	167
DS-GM	0.046	0.029	143
HZ-15	1.485	0.636	200

The obtained results enabled us to conclude, that the highest time constant value was obtained for PW ultrafiltration membrane. It proves, that in its case the permeate flux size decreases the slowest. Consequently, its life time should be longer.

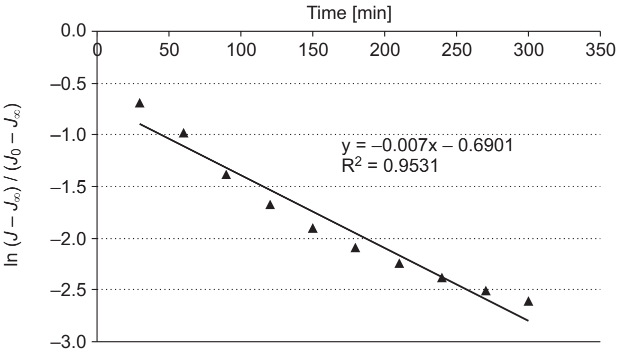

Fig. 5. Determination of characteristic time decline t_0 for ultrafiltration coke making wastewater treatment for DS-GM membrane

In the next stage we compared the changes of temporary permeate fluxes obtained in the experiments with temporary permeate fluxes determined mathematically on the basis on relaxation model that occur in the process of low-pressure filtration (Fig. 6).

It is clear that the values of temporary experimental volumetric permeates fluxes in comparison with the theoretical fluxes are lower, especially at the first stage of ultrafiltration process (PVD, PW, HZ-15), and the difference depends on the membranes structure and their resistance to a fouling process.

There was also made a comparison between volumetric permeates fluxes of the experimental average and the theoretical average (Fig. 7).

For all the membranes tested the temporary theoretical fluxes values were higher than those obtained in the low pressure filtration process. The highest medium theoretical flux was noticed for HZ-15 membrane and it was equal to $2.04 \cdot 10^{-5}$ m^3/m$^2 \cdot$ s and it was 40.5 % higher than experimental flux. DS-GM membrane was characterized by the lowest medium theoretical permeate flux: $0.034 \cdot 10^{-5}$ m^3/m$^2 \cdot$ s. It was the same as medium temporary permeate flux.

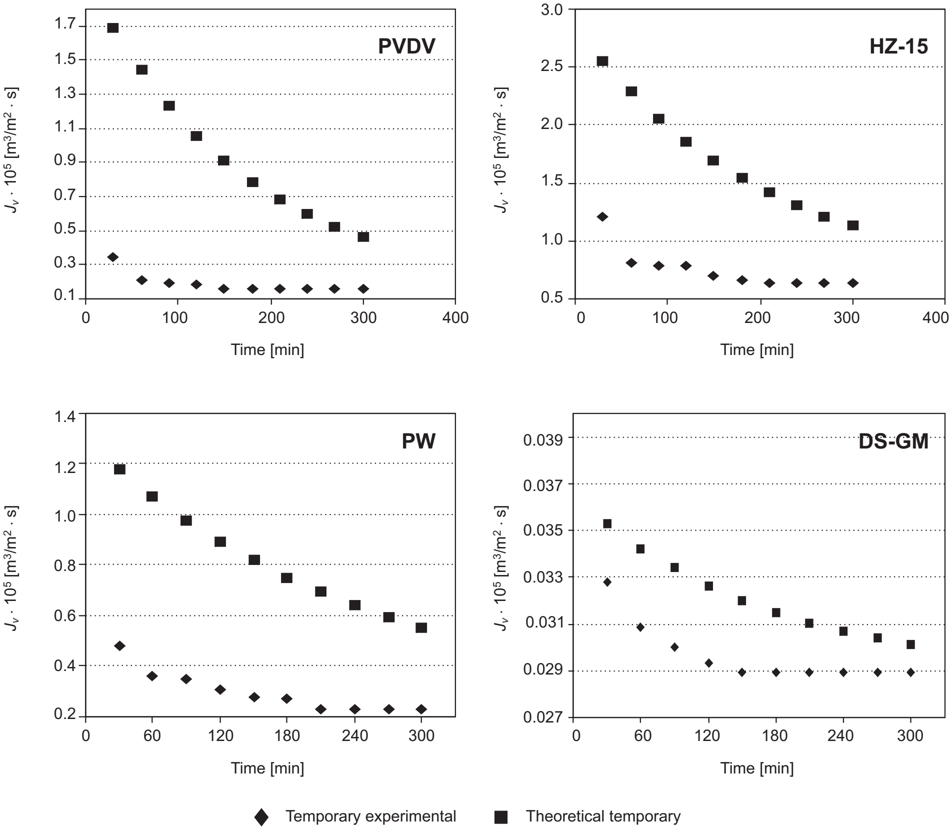

Fig. 6. Dependence of experimental and theoretical volumetric permeate flux on the coke plant wastewater ultrafiltration pre-treatment with the usage of testing membranes

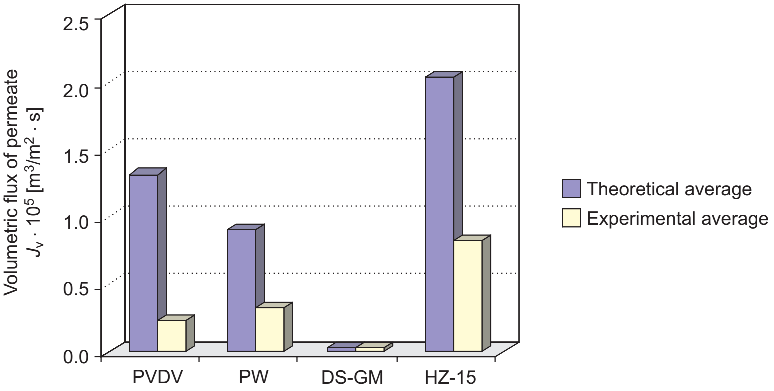

Fig. 7. Comparison between experimental and theoretical average volumetric flux of permeate in coke plant wastewater ultrafiltration treatment with the usage of commercial membranes

Higher theoretical flux values, both temporary and medium, can be explained with the fact, that the mathematical method, applied in the calculations, do not consider the complex of physical and chemical processes that occur in the membrane surface and pores. It is observed that the fouling process is more intensive for the membrane with more open structure and at the first stage of filtration.

That could lead to the conclusion that the relaxation method applied in the research which shows changes in the ultrafiltration permeate flux in coke plant wastewater treatment in a nonstationary arrangement, should be used for prediction of ultrafiltration efficiency for dense structure membranes.

Conclusion

1. The applied integrated system of ultrafiltration – reverses osmosis did not cause appropriately high degree of treatment. It did not enable to carry them to the natural receiver. The concentration of nitrogen ammonium was on the level 21 $mgNH_4^+/dm^3$. It was 2 times higher than normal. Treated wastewater can be used as technical water – for coke quenching.

2. The research showed, that temporary theoretical and average permeate of flux that were determined on the basis of relaxation model assumptions are higher than fluxes calculated in experimental way. This model, which describes changes of ultrafiltration permeate of flux in coke-making wastewater treatment, should be used to forecast ultrafiltration membranes efficiency, which have lower cut-off.

Acknowledgement

The research was carried within the project BW401/201/08.

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MODELOWANIE WYDAJNOŚCI PROCESU ULTRAFILTRACYJNEGO OCZYSZCZANIA ŚCIEKÓW KOKSOWNICZYCH Z ZASTOSOWANIEM MEMBRAN KOMERCYJNYCH

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Abstrakt: W przeprowadzonych badaniach określono efektywność oczyszczania ścieków koksowniczych w układzie zintegrowanym łączącym ultrafiltrację z procesem odwróconej osmozy. W obu procesach filtracji ciśnieniowej stosowano membrany komercyjne amerykańskiej firmy Osmonics. Stopień oczyszczenia ścieków oceniano na podstawie zmiany wartości wskaźników zanieczyszczeń, takich jak: stężenie węgla ogólnego oraz organicznego, cyjanków, fenoli, ChZT oraz azotu amonowego charakteryzujących ścieki surowe i oczyszczone. Korzystając z modelu relaksacyjnego, podjęto próbę prognozowania wydajności membran stosowanych w procesie ultrafiltracji ścieków, prowadzonym w układzie niestacjonarnym. Doświadczalnie wyznaczone wartości strumieni początkowych permeatów, strumieni nasycenia oraz wyznaczone w sposób graficzny stałe czasowe umożliwiły obliczenie teoretycznych chwilowych strumieni permeatów dla wybranych membran niskociśnieniowych.

Słowa kluczowe: ultrafiltracja, ścieki koksownicze, ciśnieniowe techniki membranowe, membrany komercyjne, model matematyczny

DOI: 10.2428/ecea.2012.19(04)049 ECOL CHEM ENG A. 2012;19(4-5):471-481

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NUMERICAL MODELING IN QUANTITATIVE AND QUALITATIVE ANALYSIS OF STORM SEWAGE SYSTEM EXTENSION

MODELOWANIE NUMERYCZNE W ILOŚCIOWEJ I JAKOŚCIOWEJ OCENIE MOŻLIWOŚCI ROZBUDOWY SIECI KANALIZACJI DESZCZOWEJ

Abstract: This paper presents the attempt of numerical modeling application to quantitative and qualitative analysis of storm-water sewer system extension in conditions of the selected urbanized catchment in city of Chelm, Poland. The USEPA's (United States Environmental Protection Agency) software SWMM 5 was applied to our studies. Three different rainfall events of various intensity and duration were studied in our research. Our calculations considered hydraulic operational conditions before and after attachment of new pipelines to the existing system. The presented analysis was based on sewage flow velocity, wastewater level along the pipelines and the load of pollutants leaving the sewer system. The visible changes in flow velocity, discharged loads of selected pollutants and sewage outflow from several join or inspection chambers were observed after development of the existing sewer system. Our studies reveals also the fact that the existing system, designed basing on Blaszczyk's formula is partially oversized, the velocity of pipes' self-purification was not assured in the some part of studied network. The quality of our observations may be reduced by the lack of model calibration.

Keywords: storm sewer, numerical modeling, network expansion, quantitative and qualitative analysis

Introduction

According to numerous problems, encountered even on the designing stage, resulting from increase of drainage area, surface runoff rate, storm water flow and loads of transported pollutants, development of existing municipal systems of storm water drainage may be treated as challenging and difficult engineering task [1].

Extension of existing storm water systems may in some cases led to improvement of hydraulic parameters of wastewater flow in drainage canals by ensuring the self-purification velocity of flow. This situation is possible due to the fact that in some

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existing storm water systems applied pipes diameters prevent autogenous pipes flushing by flowing storm sewage [2, 3].

Assumption of incorrect designing inputs during storm water network development may result in periodical water gathering in join and inspection manholes, flooding and increase of concentrations and loads of pollutants delivered to sewage receivers [4–6].

Appearance of periodical flooding should be certainly treated as disadvantageous phenomena, seriously affecting the everyday life of municipal settlement. Increase of concentrations and loads of pollutants transported by storm sewage may negatively influence the quality of water in the wastewater receiver.

Storm wastewater, as it was frequently reported in the literature, in dependence to type and manner of drainaged urbanized basin usage contain significant concentrations of pollutants: *Total Sewage Sludge* (TSS), *Chemical Oxygen Demand* (COD), *Biochemical Oxygen Demand* (BOD), *Total Nitrogen* (TN), *Total Phosphorus* (TP), heavy metals and oil derivatives [6–8]. Considering the above, in many European countries, according to European Water Frame Directive [9], the application of storm water drainage is being limited in favor of solutions based on collection and treatment of storm sewage in location of their generation [10,11].

Hence, the analysis of increased discharge of storm sewage effect on receiver's water quality conducted at the stage of storm water network extension designing seems to be requisitive.

Application of numerical modeling, allowing designing variant analyses for different rainfall events and various possible manners of network development for basins of different degree of sealing, may be a considerable help for designers and local authorities. One of the most popular pieces of software applicable in multivariate calculations is model SWMM 5 (*Storm Water Management Model*) by *United States Environmental Protection Agency* (USEPA). This model allows dynamic quantitative and qualitative calculations of storm water network operation – the quality of offered calculations were repeatedly positively verified [5, 12, 13].

Presented study focused on quantitative and qualitative analysis of storm water sewer system extension for selected municipal in Chelm city, Poland. Our researches were based on numerical calculations conducted by SWMM 5. Flow velocity of storm wastewater, canals filling height as well as concentrations and loads of TSS, TP and TN at discharge location, before and after development of stormwater network were selected as factors of our analyses.

Materials and methods

The 17.23 ha basin located in NW part of Chelm city, Poland, covering streets Szpitalna, Wygon and Ceramiczna was selected to our studies. Private housings and municipal hospital are located at the selected catchment. The existing storm water system of 1300 m length is constructed of concrete pipes of diameters from 100 to 1000 mm. Storm wastewaters are delivered to the surface retention tank of surface equal to 0.62 ha and mean depth of 1.9 m, and then diverted to the Uherka river. The proposed extension of modeled system covers new sanitation collectors in the region of

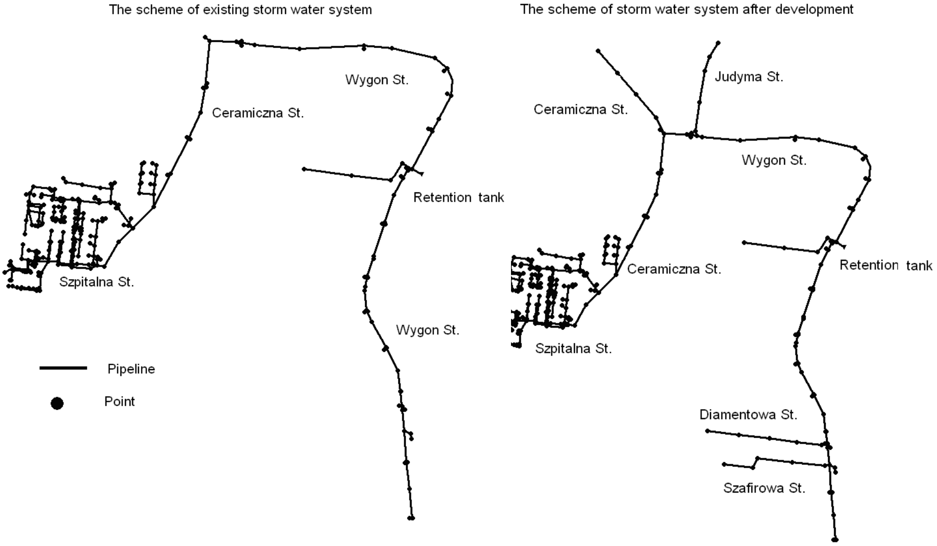

Fig. 1. Modeled storm water system – existing and after development

Szafirowa, Diamentowa, Judyma and Ceramiczna St. Development of network will result in increase of drainaged area of approximately 6.66 ha.

Numerical calculations of studied storm water network before and after extension were conducted by SWMM 5 [14]. The numerical model of existing network, based on documentation accessed by system operator, is consisting of 289 subcatchments, 284 nodes, 283 lines and sewage receiver. The model containing new collectors, in turn, consists of 404 subcatchments, 304 nodes and 303 lines and a receiver. Geometrical characteristics of the existing system and hydraulic parameters of pipes were read from the map and selected from SWMM 5 documentation [15]. The designed part of network was based on actual standards and literature guidelines [16, 17].

Our numerical calculations were conducted for the three different rainfall events (various intensity and duration of rain). Parameters of applied rainfall events, according to lack of suitable meteorological station in Chelm, were based on available literature and daily weather news: observations during 2002–2003 at measurement station in Olszanka, Poland (35 km from Chelm), reported daily sums of precipitation for the Wieprz river, Poland and archival characteristics of extreme rainfall events from 6 stations located in eastern Poland [18, 19]. Unit runoff for rain No. I of duration $t = 12$ h was accepted as 3 $dm^3 \cdot s^{-1} \cdot ha^{-1}$, rainfall event No. II $t = 1.5$ h 65 $dm^3 \cdot s^{-1} \cdot ha^{-1}$, and event No. III $t = 2.5$ h 90 $dm^3 \cdot s^{-1} \cdot ha^{-1}$.

Our qualitative numerical calculations were based on implemented in SWMM 5 equations of pollutants buildup and washoff on the catchment surface. The linear model of pollutant buildup and *event mean concentration* (EMC) model of pollutant washoff were accepted [14, 15]. Input data were applied according to literature studies for two various types of land use (residential and undeveloped) distinguished in the studied catchment [6, 20, 21].

The Event Mean Concentration is a flow-weighted average value of selected pollutant concentration. Definition of EMC may be described as follows [22]:

$$\mathrm{EMC} = \frac{\sum C_i Q_i}{\sum Q} \tag{1}$$

where: C_i – concentration of studied pollutant,
Q_i – storm water volumetric flow rate.

Input data for TSS, TP and TN modeling were also based on literature studies [6, 19, 20, 23–25].

Table 1

Models and input data applied to qualitative calculations

		Pollutant buildup		Pollutant washoff	
Model		$B = C_2 (1 - e^{C_2 t})$ B – pollutant buildup [mg · dm^{-3}] C_1 – maximum buildup possible [mg · dm^{-3}] C_2 – buildup rate constant [d^{-1}] t – time [d]		$W = C_3 \cdot Q^{C_4}$ W – concentration of pollutant in surface runoff C_3 – washoff coefficient, equal to EMC [–] C_4 – exponent, $C_4 = 1$ [-] Q – surface runoff flow rate [dm^3 · s^{-1}]	
Applied values	Residential area	TSS	$C_1 = 50$ [mg · dm^{-3}] $C_2 = 2$ [d^{-1}]	TSS	EMC = 101 [-]
		TP	Co-pollutant to TSS 58 mg TP per kg TSS	TP	EMC = 0.34 [-]
		TN	Co-pollutant to TSS 550 mg TN per kg TSS	TN	EMC = 2.64 [-]
	Undeveloped area	TSS	$C_1 = 100$ [mg · dm^{-3}] $C_2 = 3$ [d^{-1}]	TSS	EMC = 70 [-]
		TP	Co-pollutant to TSS 49 mg TP per kg TSS	TP	EMC = 0.12 [-]
		TN	Co-pollutant to TSS 460 mg TN per kg TSS	TN	EMC = 1.51 [-]

The developed numerical model of selected part of storm water network in Chelm, Poland requires empirical calibration based on multiple *in situ* measurements of the qualitative and quantitative characteristics of studied system.

Results and discussion

Possibility assessment of storm water network development in selected catchment in Chelm, Poland was conducted basing on calculated velocities of flow, collector fillings and concentrations and loads of TSS, TP and TN at the entrance to wastewater receiver, before and after the system extension. The results of our calculations were presented in Fig. 2–4 and in Table 2.

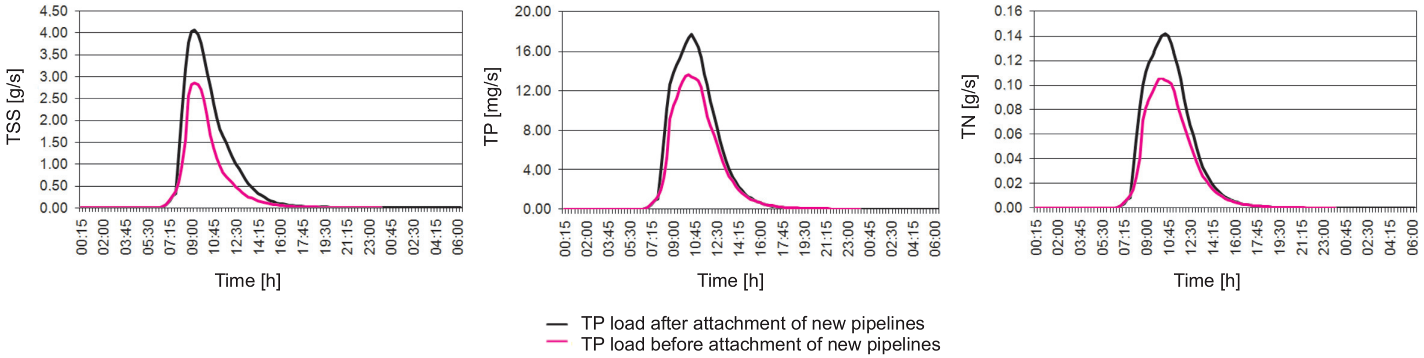

Fig. 2. Loads of TSS, TP and TN discharged to storm sewage receiver for Rainfall event No. I

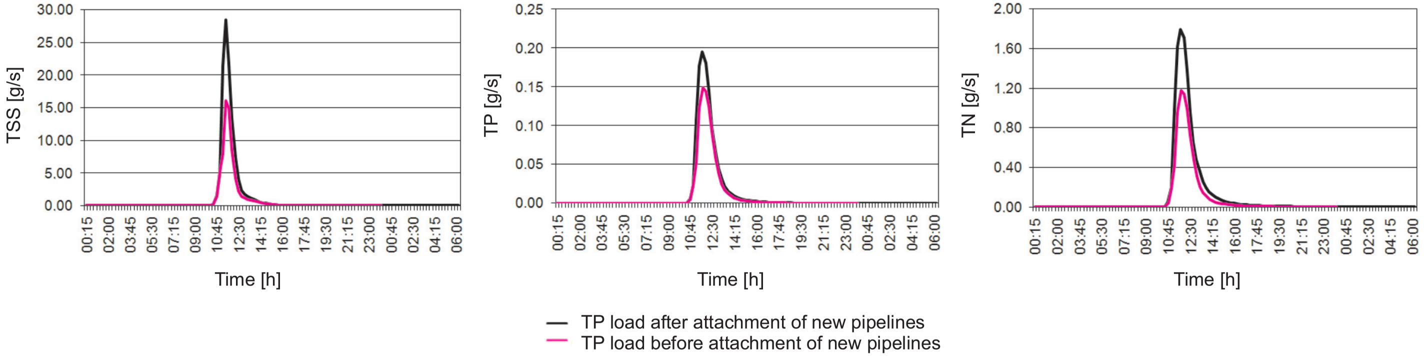

Fig. 3. Loads of TSS, TP and TN discharged to storm sewage receiver for Rainfall event No. II

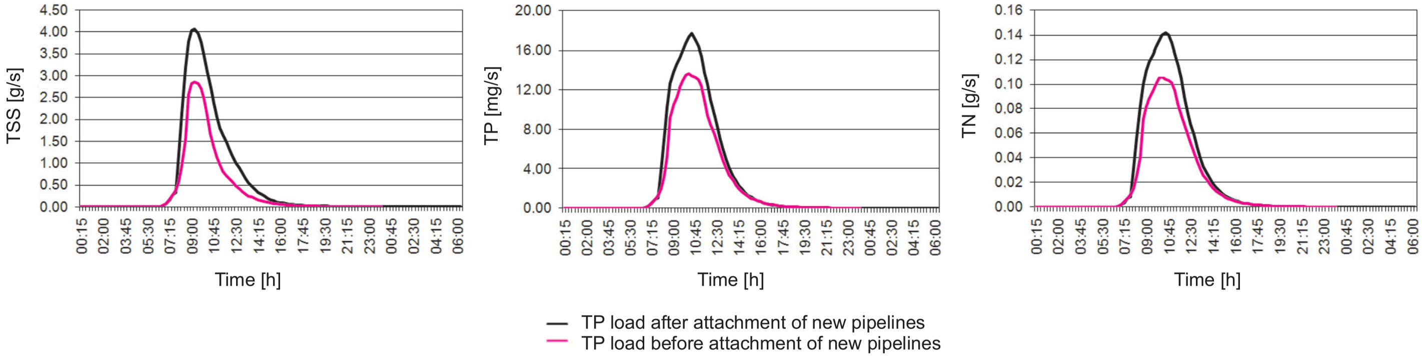

Fig. 4. Loads of TSS, TP and TN discharged to storm sewage receiver for Rainfall event No. III

Table 2

Results of quantitative and qualitative calculations for existing and planned storm water network

Studied factor	Unit	Rainfall event No. I		Rainfall event No. II		Rainfall event No. III	
		Existing network	Network after development	Existing network	Network after development	Existing network	Network after development
Flow velocity $[m \cdot s^{-1}] < 0.3$	[%]	57.80	53.13	11.66	10.89	8.48	7.92
Flow velocity $[m \cdot s^{-1}] > 0.6$	[%]	10.60	10.23	50.18	53.80	57.95	60.73
Number of chambers endangered by flooding	[-]	0	0	15	19	27	33
TSS max concentration	$[mg \cdot dm^{-3}]$	97.01	93.43	84.76	84.62	73.48	69.28
TP max concentration	$[mg \cdot dm^{-3}]$	0.34	0.31	0.32	0.29	0.32	0.29
TN max concentration	$[mg \cdot dm^{-3}]$	2.65	2.52	2.54	2.65	2.55	2.36

Our calculations, for conditions before and after development, showed that in case of rainfall event No. I velocity of flow in over 50 % of pipes is lower than $0.3 \text{ m} \cdot \text{s}^{-1}$ (Table 2). The significant improvement was observed for rainfall events No. II and III characterized by higher intensity. Calculated velocity of flow, even in case of rainfall event No. III, in 8 % of all pipes is lower than $0.3 \text{ m} \cdot \text{s}^{-1}$. After network development recommended speed of storm sewage flow higher than $0.6 \text{ m} \cdot \text{s}^{-1}$ was observed in approx. 53 % and 60 % of pipes, for variant No. II and III, respectively. However in this case, the numerous flooding were noted: for rainfall event No. II from 15 chambers in case of existing network model and 19 after development and respectively from 27 and 33 chambers for rain No. III. The clear majority of chambers endangered by flooding is located at southern part of Wygon St., at existing pipes of 0.3–0.5 m diameter and newly designed side collectors in Diamentowa and Szafirowa St. of diameter 0.3 m. Our studies showed that addition of new drainaged catchments in the region of Diamentowa and Szafirowa St. should be preceded by alternation of existing collector diameter in Wygon St.

The results of qualitative calculations of storm water network development were presented in Fig. 2–4, as well as at Table 3. The visible in all studied cases increase of transported TSS, TP and TN loads is caused, in our opinion, by increase of drainaged area and share of undeveloped and unurbanized subcatchments – bare soil parking lot and building parcels in Szafirowa, Diamentowa, Judyma and Ceramiczna regions.

The observed increase of TSS loads reached the level of, respectively, 42.96 %, 76.98 % and 72.70 % for all tested rainfall events. Increase of TP may be described by 30.15 %, 33.33 % and 31.82 % for each tested rainfall, while increase of calculated maximum loads of TN reached the level of 27.27 %, 51.69 % and 39.53 %. The decreased values of tested pollutants loads in case of rainfall event No III, in our opinion, result from the noticeable flooding observed in calculations. The excess of allowed by standards [4] value of TSS concentration in surface water delivered to the receiver was not observed. The maximum calculated value of TSS reached the level of 97.01 mg · dm^{-3}, when the maximum admissible value is equal 100 mg · dm^{-3}. Usage of open retention tank located between end of the storm drainage network and receiver to preliminary treatment of storm wastewater before discharge to the Uherka river seems to be reasonable.

Table 3

Results of qualitative modeling of tested storm water system in Chelm

Pollutants	Maximum calculated loads					
	Rainfall event No. I		Rainfall event No. II		Rainfall event No. III	
	Existing network	Network after development	Existing network	Network after development	Existing network	Network after development
TSS [g · s^{-1}]	2.84	4.06	16.07	28.44	11.21	19.36
TP [g · s^{-1}]	$13.6 \cdot 10^{-3}$	$17.7 \cdot 10^{-3}$	0.15	0.20	0.22	0.29
TN [g · s^{-1}]	0.11	0.14	1.18	1.79	1.72	2.40

Results of our qualitative calculations were compared to the reported values of observed concentrations of studied pollutants in the storm water discharged from various residential basins. Table 4 presents comparison of maximum calculated values of TSS, TN and TP concentrations for studied storm water system in Chelm, Poland to minimal, maximum and mean values of appropriate pollutants presented by literature reports [6, 22, 24, 25].

Table 4

Comparison of calculated maximum TSS, TN and TP concentrations
to values reported in literature

Catchment	Concentration [mg · dm^{-3}]		
	TSS	TN	TP
Chelm, calculated maximum values, Poland	97.01	0.34	2.65
High density residential basin, combined sewer Chongju, S. Korea [22]	33.0–2796.0 (552.2)	0.11–39,51 (11.09)	2.9–10.8 (7.2)
Residential area, Twin City, MN, USA [24]	2–3577(184)	0.43–19.4 (3.08)	0.03–9.40 (0.58)
Residential area Siosepol, Iran [6]	43–467 (161)	1.22–22.38 (6.65)	0.064–0.790 (0.274)
Birdlife, high-socio-economic single detached-dwelling area, Australia [25]	356.7 (Mean)	1.9 (Mean)	0.8 (Mean)

Comparison of concentration values presented in Table 4 shows that our results are comparable to values of tested pollutants concentrations for several various residential watersheds of different structure, populations number and inhabitants habits, presented in literature reports. Moreover, calculated maximum values of TSS, TN and TP concentrations for studied catchment in Chelm, before and after development of storm sewer system are in good agreement to EMC values for various low and medium density urban catchments compiled by Park et al [13].

Summary

Our studies proved suitability of numerical modeling application to quantitative and qualitative analysis of storm water network development in conditions of Chelm city, Poland. Thus, studies of existing and designed network operational conditions were possible. The obtained results showed that in case of low intensity rainfall events, the adverse conditions of flow occur inside the network designed on the basis of Blaszczyk's formula. The insufficient wastewater flow velocity may result in sediments deposition inside the system pipes. Simultaneously, the possibility of major flooding, significantly disturbing the life of urbanized community during the extreme rainfall events was noted during simulations of both existing and developed network.

The conducted qualitative calculations showed the clear increase of TSS, TN and TP loads after eventual development of the studied network. The excess of acceptable load of tested pollutant in storm water discharged to the receiver was not observed.

According to the lack of model calibration the presented researches should be treated as preliminary studies. We consider further studies focused on assessment of retention tank application as location of introductory wastewater treatment as well as monitoring of exiting storm water system allowing the future model calibration.

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MODELOWANIE NUMERYCZNE W ILOŚCIOWEJ I JAKOŚCIOWEJ OCENIE MOŻLIWOŚCI ROZBUDOWY SIECI KANALIZACJI DESZCZOWEJ

Wydział Inżynierii Środowiska
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Abstrakt: W pracy przedstawiono próbę zastosowania modelowania numerycznego do ilościowej i jakościowej oceny możliwości rozbudowy systemu kanalizacji deszczowej. Model wybranego fragmentu sieci kanalizacyjnej miasta Chełma wykonano w programie SWMM5. W badaniach przeanalizowano trzy warianty charakteryzujące się różną intensywnością oraz czasem trwania opadu. Obliczenia hydrauliczne wykonano dla warunków przed i po rozbudowie sieci. Przedstawiona analiza została oparta na prędkościach przepływu ścieków, napełnieniu kanałów oraz stężeniach i ładunkach transportowanych zanieczyszczeń. Po wykonaniu obliczeń symulacyjnych sieci po jej rozbudowie otrzymano wyniki, w których zaobserwowano zmiany w prędkości przepływu, napełnieniach kanałów, ładunkach badanego zanieczyszczenia. Odnotowano także w wynikach symulacji wypływ ścieków ze studzienek połączeniowych lub rewizyjnych na powierzchnię odwadnianego terenu. Przeprowadzone badania wskazują również, iż istniejący system zaprojektowany na podstawie wzoru Błaszczyka, w obecnych warunkach jest częściowo przewymiarowany. W związku z tym prędkość samooczyszczania przewodów nie została osiągnięta w znacznej części sieci. Ze względu na brak kalibracji modelu otrzymane wyniki należy traktować jako wyniki badań wstępnych.

Słowa kluczowe: kanalizacja deszczowa, modelowanie numeryczne, rozbudowa sieci, analiza ilościowa i jakościowa

DOI: 10.2428/ecea.2012.19(04)050 ECOL CHEM ENG A. 2012;19(4-5):483-493

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ANALYSIS OF POLLUTANT DISPERSION IN FLOW AROUND THE OBJECTS IN TANDEM ARRANGEMENT

ANALIZA ROZPRZESTRZENIANIA SIĘ ZANIECZYSZCZEŃ GAZOWYCH WOKÓŁ OBIEKTÓW W UKŁADZIE TANDEM

Abstract: The problem of pollution dispersion throughout atmospheric boundary layer has grown in importance since human activity has become so intense that it started having considerable impact on natural environment. The level of concentration of pollutants has escalated, particularly in urban areas and it impacts on their inhabitants.

The paper presents the results of the complex research program aimed at understanding a character of the flow field in neighborhood of bluff-bodies immersed in a boundary layer and characteristics of pollutants dispersion in that area. Analysis of gas pollutants dispersion process requires in-depth identification of the structure of flow around the buildings. The analysis has been performed for the 3D case of two in-line surface-mounted bluff bodies, arranged in tandem, which were placed with one face normal to the oncoming flow. The mean concentration profiles of tracer gas (CO_2) for various inter-obstacle gaps were measured in wind tunnel. Characteristic feature of flow field around groups of buildings in urban areas is high level the unsteady phenomena resulting from itself character of the wind or from the interference of the wake flow connected with a process of vortex shedding. This is the factor affecting process of the dispersion of pollutants in the built-up area acting more complex the mechanism of propagate of small parts explained on the basis of processes of advection and turbulent diffusion. The local characteristics of flow were obtained by the use of commercial CFD code (FLUENT).

Keywords: buildings arrays, pollutant dispersion, experimental and numerical modelling

Introduction

The problem of pollution dispersion throughout atmospheric boundary layer has grown in importance since human activity has become so intense that it started having considerable impact on natural environment. The level of concentration of pollutants has escalated, particularly in urban areas and it impacts on their inhabitants [1, 2].

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Ensuring adequate air quality requires proper aeration of these areas. Its efficiency depends mainly on wind direction, configuration of buildings and locations of emissions sources. The process of pollution dispersion is mainly influenced by mechanisms of mass diffusion, caused by concentration gradients and advection which transfers pollutants in flow direction through mean air movement. The specific flow conditions generated around bluff bodies arrangement make it possible to study the gas pollutant dispersion for the case of very complex velocity field typical for built environment. Curved streamlines, sharp velocity discontinuities, high level flow oscillations and non-homogenous turbulence disperse effluents in a complicated manner related to source configuration and object geometry [3]. Improvement in air quality on a local scale and limitation of effect of pollution on human health requires consideration of all the listed factors.

An important role in increasing knowledge about dispersion processes that occur in the atmosphere is played by the investigations carried out inside wind tunnels. They also deliver data necessary for verification of the results obtained by means of numerical modelling. During model testing of environmental aerodynamics, actual shapes of ground object are typically replaced with their simplified versions. In the case of buildings, this usually means cuboids of different height. The goal of the present work was to determine impact of object configuration, level of their ‘immersion’ in boundary layer and location of emission source on dispersion of the emitted gas marker [4, 5].

This paper presents the experimental test of the qualification of the relation between a structure of the flow field in complex urban terrain (in the built-up area) and characteristics of pollutants dispersion. The aim of this work was to determine the impact of objects configuration, their degree of “immersion” in the boundary layer and location of emission source for the spread of the tracer gas emitted in the vicinity of two rectangular blocks in tandem arrangement.

Methods of analysis

The program of this study consists of: wind-tunnel measurement of the mean concentration profiles in the inter-body gap for different body “immersion” in boundary layer, comparison of concentration field with aerodynamic characteristics (obtained as a result of numerical simulation performed at the Institute of Thermal Machinery of the Czestochowa University of Technology (ITM CzUT). The numerical simulation was performed with the use of k-ε turbulence model in realizable version. The flow conditions of the computational domain were the same as those in the experiment. The boundary conditions imposed at the inlet to the computational domain were the same as those obtained from the wind-tunnel experiment.

The experiments were carried out in an open-circuit wind tunnel (Fig. 1). The test section was 400 × 400 mm square and 4000 mm long. All the measurements were carried out for the $Re_D = 3.4 \cdot 10^4$ based on the free stream velocity $U_\infty = 13$ m/s and the cube width D = 0.04 m. Figure 2 presents the geometries of the analyzed cases of two obstacles, where H_1/H_2 describes their height ratio and S/D = 2.5 (constant) the distance between them.

Analysis of pollutant dispersion in flow around the objects in tandem arrangement

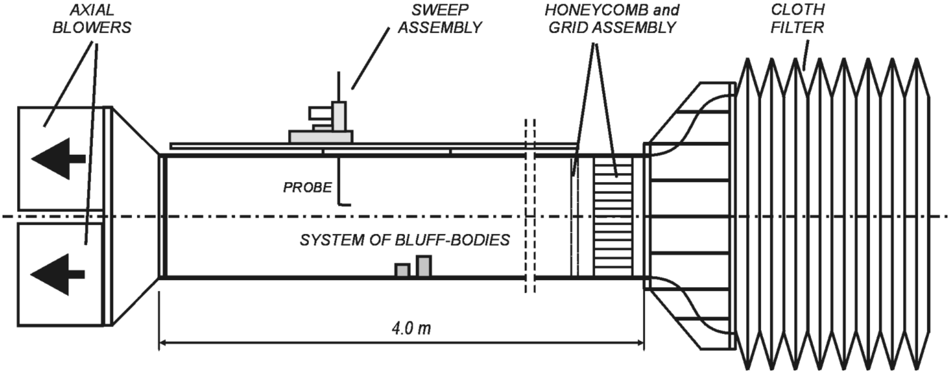

Fig. 1. Two-dimensional channel flow with the system of bluff-bodies

The source of emission of carbon dioxide used as a gas marker during the investigations was a brass pipe with inner diameter 3 mm, located before the windward object at the distance of 1.5 D. CO_2 flow rate was maintained at constant level Q = 5 dm^3/min, which produced output speed of U_{CO_2} = 11.8 m/s. In order to measure mean concentration of gas marker a Guardian plus CO_2 Analyzer was used. Measurement probe in the form of aluminium pipe with inner diameter of 2.6 mm was connected with analyser inlet by means of supple pipe. Location of the source and the measurement probe in relation to the investigated arrangement of the objects as well as the assumed coordinate system are presented in the Fig. 2.

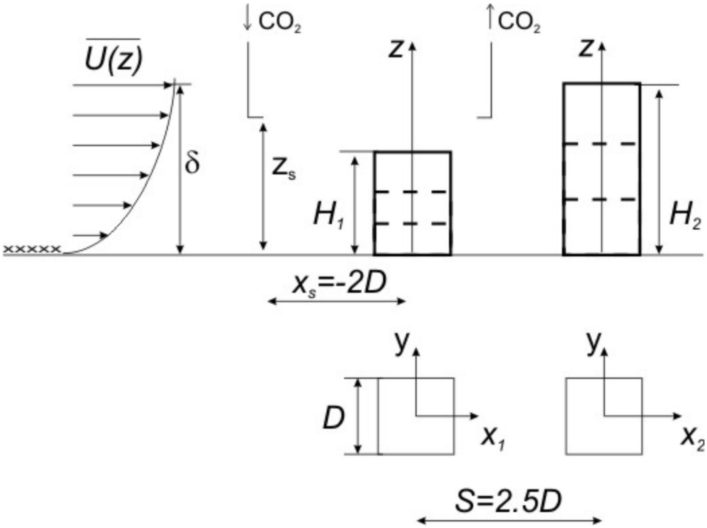

Fig. 2. Schematic presentation of the set-up and nomenclature

The measurements were carried out for configurations of two elements with different height, aligned in one line. The results of testing presented in this work relate to a fixed ratio of object height $H_1/H_2 = 0.6$ and three values of their "immersion" in boundary layer $H_2/\delta = 0.3$; 0.6 and 1.0.

For all the considered configurations, an identification of the structure of flow by means of surface oil visualization was performed. Measurements of concentration CO_2 were taken in the gap between the elements in measurement cross-sections $x/D = 0.5$; 0.625; 0.75; 0.875; 1; 1.25 both in system axis and along the edges of external objects, for two different positions of emission source $z_S = 0$ and H_1 situated at the distance of 1.5 D in front of the windward object. In order to visualize the flow-modifying impact of the leeward object, some measurements of concentration CO_2 profiles were also taken for a single object.

Discussion of the results

Analysis of gas pollutants dispersion process requires in-depth identification of the structure of flow around the buildings. The flow structure around three-dimensional bluff-body located on the surface with formed boundary layer is characterized by a high level of complexity. In the presented spatial diagram of flow line (Fig. 3), the following characteristic areas in this type of flow can be distinguished: area of the horseshoe

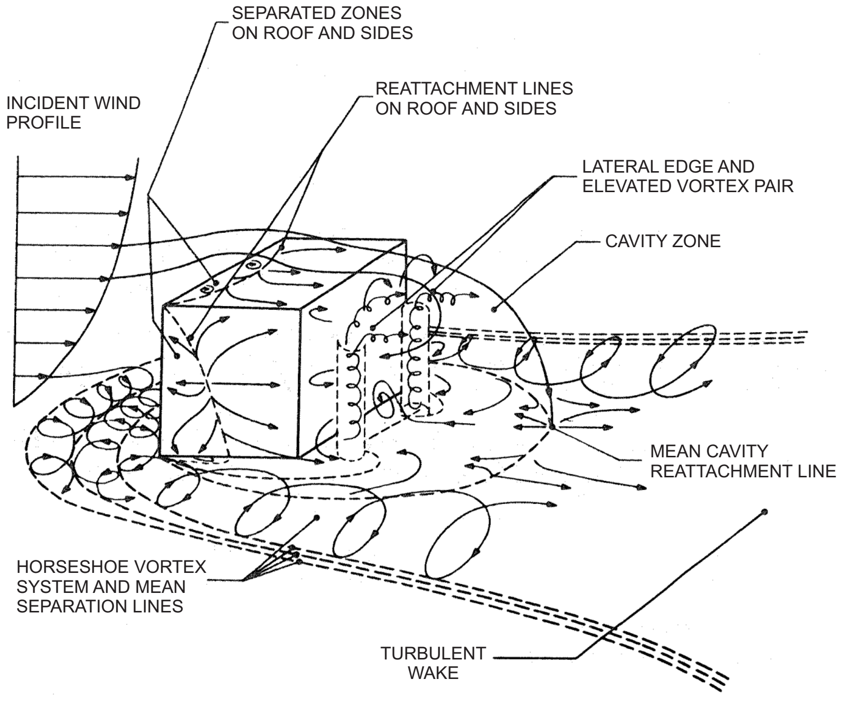

Fig. 3. Model of flow near a sharp-edged building normal to deep boundary layer [7]

vortex forming in front of the object upper flow, close and farther wake zones. According to Hunt [6] interpretation, flow around the object is composed of a range of separation and adherence points classified as singular nodal and saddle points. The zones typical of flow around cuboids are clearly visible in the image (see Fig. 3) being the result of oil surface visualization. One can distinguish here a horseshoe vortex, whose name derives from its characteristic shape, and post-edge vortices, located in close distance from rear side of the object. White spots in the image are identified as the areas of flow stagnation. However, black color is associated with areas of high flow rate such as wide band of lateral flow, which extends over the considerable distance behind the object.

Object impact zone, *ie* area where velocity field is strongly disturbed by the presence of the obstacle, changes considerably if another object is placed in the aerodynamic wake. The case under consideration in this work concerns tandem arrangement which is characterized by H_1/H_2 parameter, which is conducive to occurrence of downwash effect. This effect consists in washing of front side of the leeward object with large air masses, which results in strong air circulation in the area between objects, which determines flow structure between them.

This situation is presented in Fig. 4, which gives a comparison of surface oil visualization (Fig. 4a) within the numerical results of mean velocity distributions (Fig. 4b) obtained with the steady-state (RANS) method for tandem arrangement of two cuboids for three values of their "immersion" in boundary layer $H_2/\delta = 0.3$; 0.6 and 1.0. Disturbing impact of the second object, expressing particularly in location of the couple of post-edge vertices behind windward object and changes in the shape of lateral flow is distinctly visible. The level of modification of flow around the analysed arrangement of objects of tandem type depends on many factors. Change in height of the elements of the arrangement impacts on changes in the immersion parameter in boundary layer. As results from Fig. 4, this parameter has significant impact on the flow structure.

The biggest changes in flow field are observed in the area between objects. Rise the object height in relation to layer thickness causes rise in impact of windward object and increase in width and length of recirculation zone and extension of the area taken by vortices. Aerodynamic wake of the leeward object is wider than the width of its horseshoe vortex of the windward object. Spacing in lateral edge vortices behind windward object is bigger than in lateral edge vortices behind leeward object and it rises with the object height.

Such a statement can also be confirmed by the distributions of streamwise mean velocity component in that area presented in Fig. 4b. The level of mean velocity in the inter-body space seems to be important for the recognition of interference mechanisms in flow system considered. The data juxtaposed in Fig. 4a refer to the changes of velocity flow field observed on Fig. 4b for different values of parameter H_2/δ. As has been mentioned previous the ratio of the objects height to the incoming boundary layer thickness H/δ has an important influence on the flow structure, and on the separation regions upstream and downstream the obstacle.

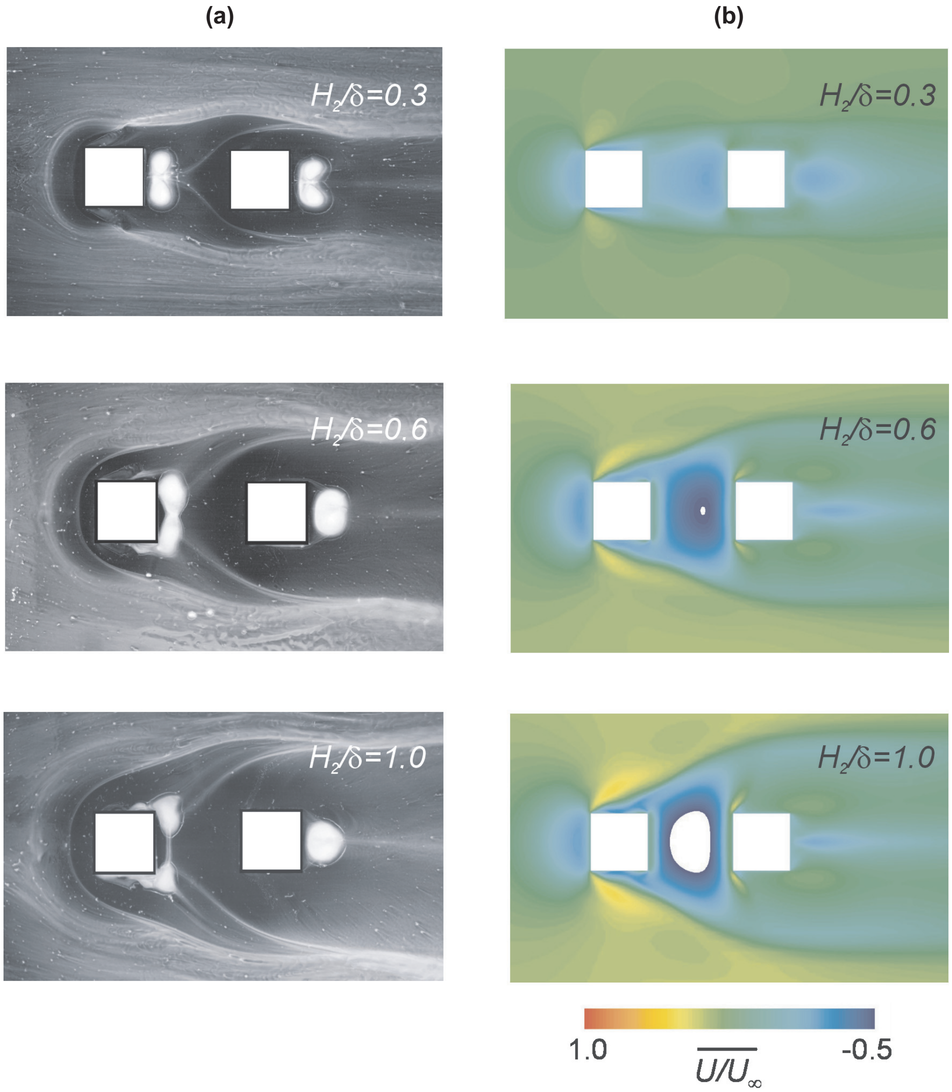

Fig. 4. The surface flow patterns obtained with oil-film technique (a) and distributions the streamwise component of mean velocity on pedestrian level (b) around configurations of two elements ($S/D = 2.5$ $H_1/H_2 = 0.6$) for different the immersion parameter $H_2/\delta = 0.3$; 0.6; 1

Scope and method of the objects interaction on their wind environment changes as a function of distance from the ground. It is clearly visible on the distributions of the streamwise mean velocity component for example configuration (Fig. 5). Closer to the ground, on pedestrian level ($z/H_2 = 0.008$) observed very different velocity flow field with strong gradients. With increasing distance from the ground impact zone of objects arrangement on the flow narrows and U/U_∞ approaching unity.

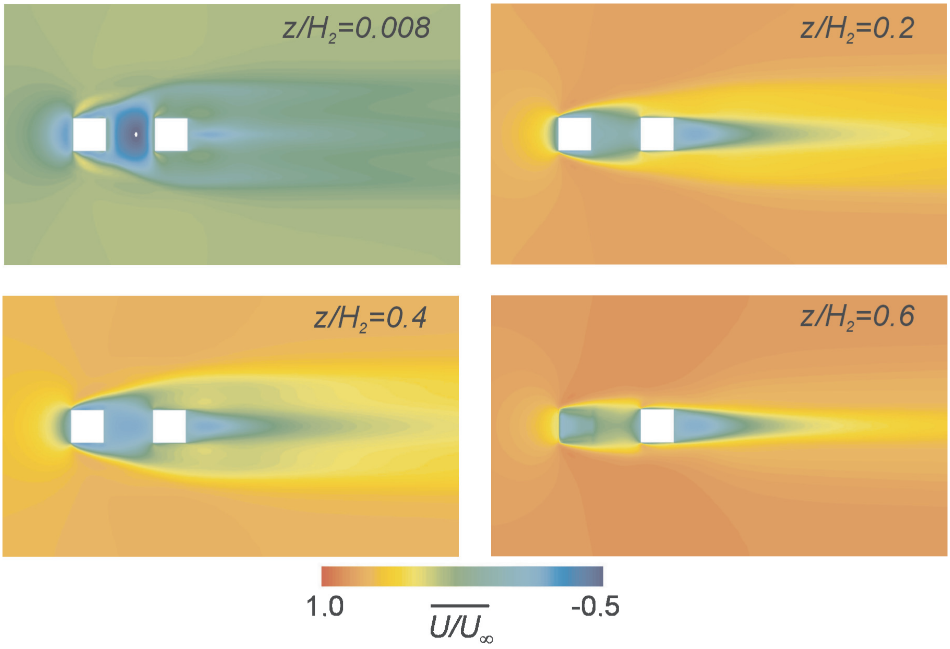

Fig. 5. Distributions of the longitudinal component of mean velocity for objects in tandem arrangement ($S/D = 2.5$ $H_1/H_2 = 0.6$) as a function of distance from the ground

The observed modifying impact of interaction between the objects in tandem arrangement is reflected in the results of measurements of concentration of the gas marker emitted in their environment. Figure 6 presents cross-sectional distribution of concentration in the gap between objects for three of the considered configurations.

It is remarkable that highest values of concentration of gas marker can be observed for $H_2/\delta = 0.3$. The effect of downwash manifests strongest in the case $H_2/\delta = 1$. Impact of the leeward object on flow field around the tested arrangement, increasing with the height of the objects, maintaining the same distance between each other, is undoubtedly connected with the fact that the increase in windward object height causes that leeward object gets more and more into the aerodynamic wake of the first one. The scope of the close wake behind the cuboids object increases proportionally to its height, which is caused by higher, in the case of higher elements, kinetic energy of the upper flow that delays its adhesion to the base [3]. In the case of emission source being located at the height of windward object, gas marker is moved mainly through upper flow, which is reflected in distribution of its concentration shown in the Fig. 6. Lower kinetic energy and, in consequence, lower flow rate, results in higher concentration of gas marker in the zone above the windward object. Ascent of the trail of carbon dioxide for the objects with highest level of immersion ($H_2/\delta = 0.3$) reaches three heights of the windward object and decreases with the height of the objects. Analysis of the carbon dioxide concentrations along the rear wall of the windward object (Fig. 6) reveals that for each of the three cases there is a minimum concentration in its neighborhood, in roughly half

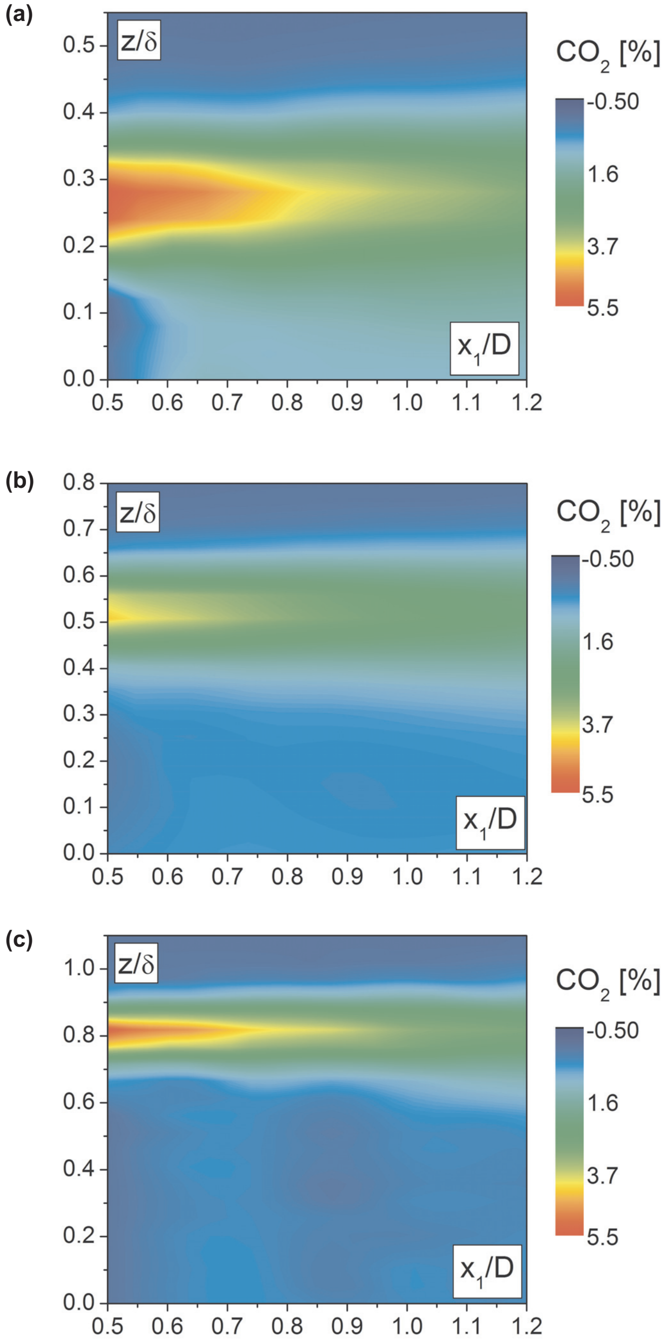

Fig. 6. Distribution of mean concentration CO_2 ($z_S = H_1$; $y/D = 0$) in the inter-obstacle gap for different the immersion parameter (a) $H_2/\delta = 0.3$, (b) $H_2/\delta = 0.6$ and (c) $H_2/\delta = 1$

of the building height. Moreover, in the case of the traverse that crosses the line connecting axes of post-edge vortices, which occurs for the arrangement with immersion $H_2/\delta = 1$, one can see a distinct reduction in concentration CO_2 in upper half of the building. Slightly higher concentration of the gas marker next to the base is probably caused by additional contribution of horseshoe vortex to its transport.

Impact of the location of emission source on the dispersion of marker gas in the environment of object arrangement of tandem type was analysed for two source heights, $z_S = 0$ and H_1. Figure 7 presents distribution of concentration in the gap between elements for the source located at the height of the windward object (black lines) and for emission source located on the base (red lines). The measurements were taken in the

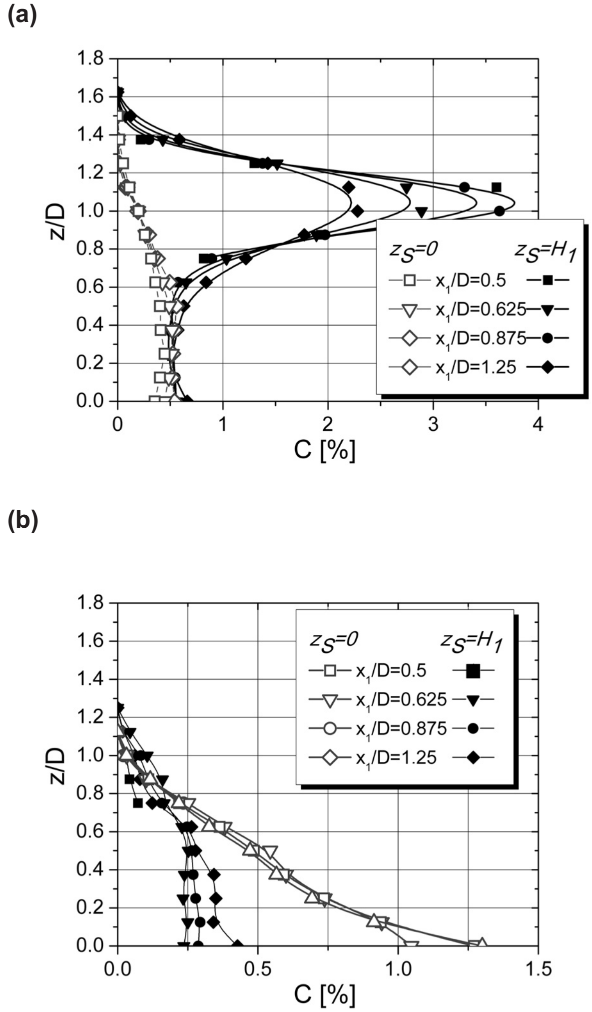

Fig. 7. Tracer gas concentration in the gap between objects in tandem configuration and single windward object for parameters $H_2/\delta = 0.6$; $z_S = 0$ and $z_S = H_1$; a) $y/D = 0$, b) $y/D = 0.5$

arrangement axis y/B = 0 (Fig. 7a) and also along the outside edges of its elements y/B = 0.5 (Fig. 7b).

For different heights of emission sources a diametrically opposite concentration CO_2 distribution was obtained. In the case of source located at the height of windward object, a dominating contribution to the transport of gas marker is from upper flow while for $z_S = 0$ value marker gas is moved mainly through surface vortex structures. Comparison of the results for both objects and single object indicates modifying impact of leeward object on the concentration field. This impact is essential and correlates with images of flow shown in the Fig. 4.

The differences appear practically for each location of the source and each measuring traverse. The highest values of marker gas in tandem arrangement axis (y/D = 0) – higher for $z_S = H_1$ than for the source located on the base – are observed in the area above the height of windward building. In the case of the measurements along the outside edges (y/D = 0.5), maximal concentration of CO_2 values appear in the base.

Conclusions

In present study the influence of bluff-bodies arrangement on computational velocity signals in flow around the prisms configuration in tandem arrangement has been discussed for analysis of pollutant dispersion in bodies neighborhood. The main attention of this paper was to determine the impact of objects configuration, their degree of "immersion" in the boundary layer and location of emissions sources for the spread of the tracer gas emitted in the vicinity of two rectangular cubes in tandem arrangement. The obtained results revealed that characteristics of the velocity field can be affect on the dispersion of pollutants in the built-up area.

The presented results show how important for ensuring adequate air quality, proper formation of wind-related environment of ground objects is.

Acknowledgements

The computations were performed at Academic Computer Centre CYFRONET AGH in Kracow (grant No. MNiSW/SGI3700/PCzęst./024/2009), which we gratefully acknowledge. This paper was supported by the State Committee for Scientific Research under Grant No. WZ-1-103-701/08 titled "Modeling of wind environment as part of urban planning".

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ANALIZA ROZPRZESTRZENIANIA SIĘ ZANIECZYSZCZEŃ GAZOWYCH WOKÓŁ OBIEKTÓW W UKŁADZIE TANDEM

Instytut Maszyn Cieplnych
Politechnika Częstochowska

Abstrakt: Problem rozprzestrzeniania się zanieczyszczeń w przyziemnej warstwie atmosfery nabrał znaczenia, gdy działalność człowieka stała się na tyle intensywna, że zaczęła wywierać istotny wpływ na stan środowiska naturalnego. Poziom koncentracji zanieczyszczeń nasilony jest zwłaszcza w obszarach zurbanizowanych, oddziałując na jego mieszkańców. W pracy przedstawiono wyniki modelowych badań dotyczących procesu dyspersji zanieczyszczeń gazowych w strefie zabudowanej. Ich celem było określenie wpływu konfiguracji obiektów, stopnia ich „zanurzenia” w warstwie przyziemnej, a także położenia źródła emisji na rozprzestrzenianie się znacznika gazowego (CO_2) emitowanego w ich otoczeniu ze źródła skupionego. Analiza procesu dyspersji zanieczyszczeń gazowych wymaga dokładnego rozpoznania struktury przepływu wokół elementów zabudowy. Badany układ typu tandem stanowiły dwa trójwymiarowe modele budynków o różnych wysokościach ustawione w jednej linii. Profile koncentracji gazu znacznikowego (CO_2) dla różnych konfiguracji obiektów zmierzono w tunelu aerodynamicznym. Cechą szczególną pól prędkości w otoczeniu grupy opływanych budynków jest wysoki poziom niestacjonarności wynikający zarówno z samego charakteru wiatru, jak i z faktu generowania przez obiekty zjawisk periodycznych związanych z procesem schodzenia wirów. Jest to czynnik, który oddziałuje na proces dyspersji zanieczyszczeń w obszarze zabudowanym, czyniąc jeszcze bardziej złożonym mechanizm rozprzestrzeniania się cząstek, tłumaczony na podstawie procesów adwekcji i turbulentnej dyfuzji. Wykorzystywane w pracy charakterystyki aerodynamiczne opływu budynków uzyskane zostały z wykorzystaniem programu FLUENT.

Słowa kluczowe: dyspersja zanieczyszczeń, układ budynków, modelowanie eksperymentalne i numeryczne

DOI: 10.2428/ecea.2012.19(04)051 ECOL CHEM ENG A. 2012;19(4-5):495-498

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COPPER AND ZINC CONCENTRATIONS IN SOIL, PASTURE SWARD AND BLOOD PLASMA OF BEEF CATTLE

STĘŻENIE MIEDZI I CYNKU W GLEBIE, MURAWIE PASTWISKA ORAZ W OSOCZU KRWI BYDLĘCEJ

Abstract: The objective of this study was to compare concentrations of copper and zinc in soil, pasture sward and blood plasma of extensive reared Aberdeen Angus bulls and heifers on a farm in the foothills of the Orlicke Mountains. We sampled soil, pasture sward from pasture areas and blood from 22 bulls and 22 heifers in the period from birth to weaning at regular intervals (81, 151, 189 and 273 days of age). Concentrations of copper and zinc were analysed. Significant relationships ($p < 0.05$) was noted between soil and pasture copper concentrations ($r = 0.74$), pasture and blood plasma copper concentration ($r = 0.29$). No other significant correlation between monitored parameters was found.

The indicators determined in this study can be used to specify the health and nutritional status of animals reared in the extensive suckling cows systems more detailed.

Keywords: beef cattle, iron, copper, zinc, soil, pasture, blood plasma

Among different environmental factors, soil plays a vital role in cattle production and health because cattle appease their nutrient needs from the feed and fodder, which in turn obtain nutrients from the soil. The role of soil and nutritional quality of plants with respect to the health and production of livestock is very important and varies from place to place [1]. Plants are the basic and potential source of food for animals; ultimately the nutritional values of plants are of central importance in determining the plants and human health. Herbs are an important source of delivering minerals to grazing livestock in extensive and low-input situations. At the same time mineral deficiencies can depress forage digestibility and herbage intake and ultimately decrease livestock production efficiency [2]. The uptake of minerals and particularly trace minerals by plants can provide important information on environmental contamination and requirements of

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ruminants [2, 3]. Plants absorb minerals from soil as well as from surface deposits on parts of plants exposed to polluted areas [2]. Information on mineral levels of forages are very important to identify what measures should be taken to improve the nutritional status of grazing livestock. Seasonal variation affects livestock seasonal production in different regions of the world by affecting forage dry matter accumulation [4, 5].

Because trace elements that constitute an important part of animal nutrition have unique roles in mammals, their deficiencies can adversely affect animal health [6]. Copper, one of the trace elements, is involved in numerous physiological functions such as hemoglobin formation, iron metabolism, and connective tissue metabolism [7]. Copper deficiency is associated with numerous clinical signs, including anaemia, severe diarrhoea, weight loss or diminished weight gain, epiphyseal enlargement, change in hair colour, neonatal ataxia, and infertility [8]. Several biochemical and physiological changes have been reported in Zn deficient animals, including an early decrease in serum alkaline phosphatase, then a loss of appetite, followed by poor growth and reduced feed efficiency [9, 10].

The objective of this study was to characterize the mineral status of soil and forage system in relation to blood minerals concentration of grazing beef cattle.

Materials and methods

The experiment was conducted in pasture areas in the foothills of the Orlicke Mountains (Czech Republic). The elevation in this area is around 500 m a.s.l., and the total annual precipitation is on average 728 mm per year. Twenty-two grazing bull and heifers were selected for observation from birth to weaning. Sampling of soil, forage and blood plasma were provided at regular intervals (81, 151, 189 and 273 days of the animals age). The representative soil and forage samples were collected randomly. Composite forage samples weighing about 400 g were made from combined clippings from a sampling position. Soil samples were taken from below the clipped swards at 0–30 cm depths, using a soil sampler.

The soil samples were extracted in 2 mol · dm^{-3} HNO_3 according to [11]. Forage samples were dried in an oven at 60 ^{o}C and decomposed in the microwave system Ethos 1 (Milestone, Italy) in the mixture of nitric(V) acid and hydrogen peroxide. The contents of Zn and Cu were determined on high resolution continuum source atomic absorption spectrometer ContrAA 700 (Analytik Jena, Germany) by using flame atomization. Blood plasma concentration of Cu and Zn was measured on an XT20i automatic analyser (Thermo Fisher Scientific, Finland) using common commercial sets (Biovendor-Laboratorní medicína, Czech Republic).

Statistical analysis of the obtained data was performed using the STATISTICA 8.0 programme. Single-factor analysis of variance was used for factor time. ANOVA was followed by post-hoc Fisher's LSD test for pair-wise comparisons, when appropriate. Evaluation of the interdependence between the soil, forage and animals minerals concentration was conducted using a correlation coefficient at the level of probability ($p < 0.05$).

Results and discussion

The mean soil copper concentration was much higher than the critical level of 0.3 mg · kg^{-1} as stated by some of authors [12, 13]. Winter season copper level in soil was significantly higher than summer season level. In all pastures, the soil Cu level was lower during summer than winter season, according to [2]. Most of the soil samples form pastures had zinc levels higher than the critical level 2.5 mg · kg^{-1} [13]. The effect of season on soil zinc level was not profound and variation was minor. Forage copper and zinc contents rose significantly ($p < 0.05$) with the aging of forage plants from spring to summer season, corresponding to [2]. Soil concentrations of those elements were found to be high, but in forage was determined low content, especially first half of monitoring, compared with [14]. It could be due to antagonism among other mineral elements such sulphur, calcium etc., in the uptake of copper and zinc by forage [2]. Also [12] suggest cattle requirements of zinc between 20 and 40 mg · kg^{-1}. Copper concentrations in blood plasma of bulls and heifers changed slightly during the survey. Significant increasing was found at the end of experiment. The average values fluctuated between 8.09 and 13.21 μmol · dm^{-3}. Significant decreasing of plasmatic zinc concentrations were determined in bulls and heifers from beginning to end of observation. The range of average values was between 9.39 and 15.18 μmol · dm^{-3}. Copper and zinc blood plasma concentration were in physiological range according to [15].

In our study significant relationships ($p < 0.05$) was noted between soil and pasture copper concentrations ($r = 0.74$), pasture and blood plasma copper concentration ($r = 0.29$). Also [16] found high correlation between soil and fodder ($r = 0.823$) and between fodder and cattle ($r = 0.885$). Contrary those authors, we did not record significant correlation between forage and blood plasma zinc content.

Table 1

Soil-forage-cattle blood plasma correlation of copper and zinc concentrations

Mineral		Soil-forage	Forage-blood plasma	Soil-blood plasma
Cu	correlation value	**0.74**	**0.29**	0.54
	P value	< 0.05	< 0.05	0.092
Zn	correlation value	0.37	0.58	0.34
	P value	0.335	0.273	0.181

Conclusion

Evaluation of copper and zinc in the forage or other diet for ruminants has limited diagnostic value. It can be concluded, from the results of the present study, that cattle reared under extensive production system in foothills of the Orlicke Mountains were not deficient in Cu and Zn minerals. The present study established some relationship between soil, forage, and cattle.

Acknowledgement

The present study was supported by the National Agency for Agricultural Research, Ministry of Agriculture of the Czech Republic, project no. QH71156 and Ministry of Education, Youth and Sports, project np. 2B08039.

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STĘŻENIE MIEDZI I CYNKU W GLEBIE, MURAWIE PASTWISKA ORAZ W OSOCZU KRWI

Abstrakt: Celem pracy było porównanie stężenia miedzi i cynku w glebie, runi pastwiskowej oraz osoczu krwi buhajów i jałówek rasy Aberdeen Angus, hodowanych w gospodarstwie u podnóża Gór Orlickich. Badano glebę, murawę pastwisk oraz krew 22 byków i 22 jałówek w okresie od urodzenia do odsadzenia w regularnych odstępach czasu (81, 151, 189 i 273 dni życia). W pobranych próbkach oznaczono stężenie miedzi i cynku. Istotne korelacje ($p < 0,05$) zaobserwowano pomiędzy stężeniem miedzi w glebie i w paszy ($r = 0,74$) oraz w paszy i w osoczu krwi ($r = 0,29$). Nie stwierdzono żadnych innych istotnych korelacji pomiędzy monitorowanymi parametrami. Parametry określone w tym opracowaniu mogą być używane do bardziej szczegółowego określenia stanu zdrowia i odżywienia zwierząt hodowanych.

Słowa kluczowe: bydło, żelazo, miedź, cynk, gleba, pastwiska, osocze krwi

Varia

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[2] Fasino CR, Carino M, Bombelli F. Oxidant profile of soy standardized extract. In: Rubin R, Stryger CS, editors. Joint Meeting 2001 – Book Abstracts ‘2001 Year of Natural Products Research’. New York: Harper and Row; 2001.

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