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CONTENTS

VARIA

SPIS TREŚCI

VARIA

Anna BUCIOR[1] and Gorzysław POLESZCZUK[1]

WHAT HAPPENS IN THE WATERS OF THE WARNOWO, RABIAZ, CZAJCZE AND DOMYSLOWSKIE LAKES IN THE WOLIN NATIONAL PARK DURING SUMMER STAGNATION?

CO SIĘ DZIEJE W WODACH JEZIOR WARNOWO, RABIĄŻ, CZAJCZE I DOMYSŁOWSKIE W WOLIŃSKIM PARKU NARODOWYM PODCZAS STAGNACJI LETNICH?

Abstract: In 2007, 2008 and 2010, water temperature and water saturation by O_2 profiles were determined in summer in the Warnowo, Rabiaz, Czajcze and Domyslowskie Lakes interconnected by inlets being situated within the Wolin National Park in the Warnowo-Kolczewo Lake District on the Wolin Island. The occurrence of homothermy and practically constant water oxygenation from 0.5 m below the surface to 0.5 m above the bottom, with the waters under analysis being characterised by strong oxygen deficiency which differed however in consecutive lakes. The results of determinations of general parameters, biogenic substance concentrations and mineralisation indices also showed small but yet clear differences in the chemistry of the lakes under analysis, which was connected with different anthropogenic pressure on respective ecosystems and limitation of the water flow through consecutive lakes down the drainage basin. It was showed that the occurrence of low water saturation by O_2 in the body of water of the lakes under analysis was connected with progressive dystrophication of the analysed ecosystems, being manifested as exuberant growth of rush vegetation and, first of all, floating plants.

Keywords: lakes, water saturation by O_2; lakes: Warnowo, Rabiaz, Czajcze and Domyslowskie; Wolin National Park

Introduction

During summer stagnation, a characteristic profile of changes in water-dissolved oxygen concentration for a given lake ecosystem is being formed in lake waters as depth increases. In eutrophic lakes with clearly marked epilimnion and the metalimnion and hypolimnion being more or less sheltered from the wind, the oxygen curve takes

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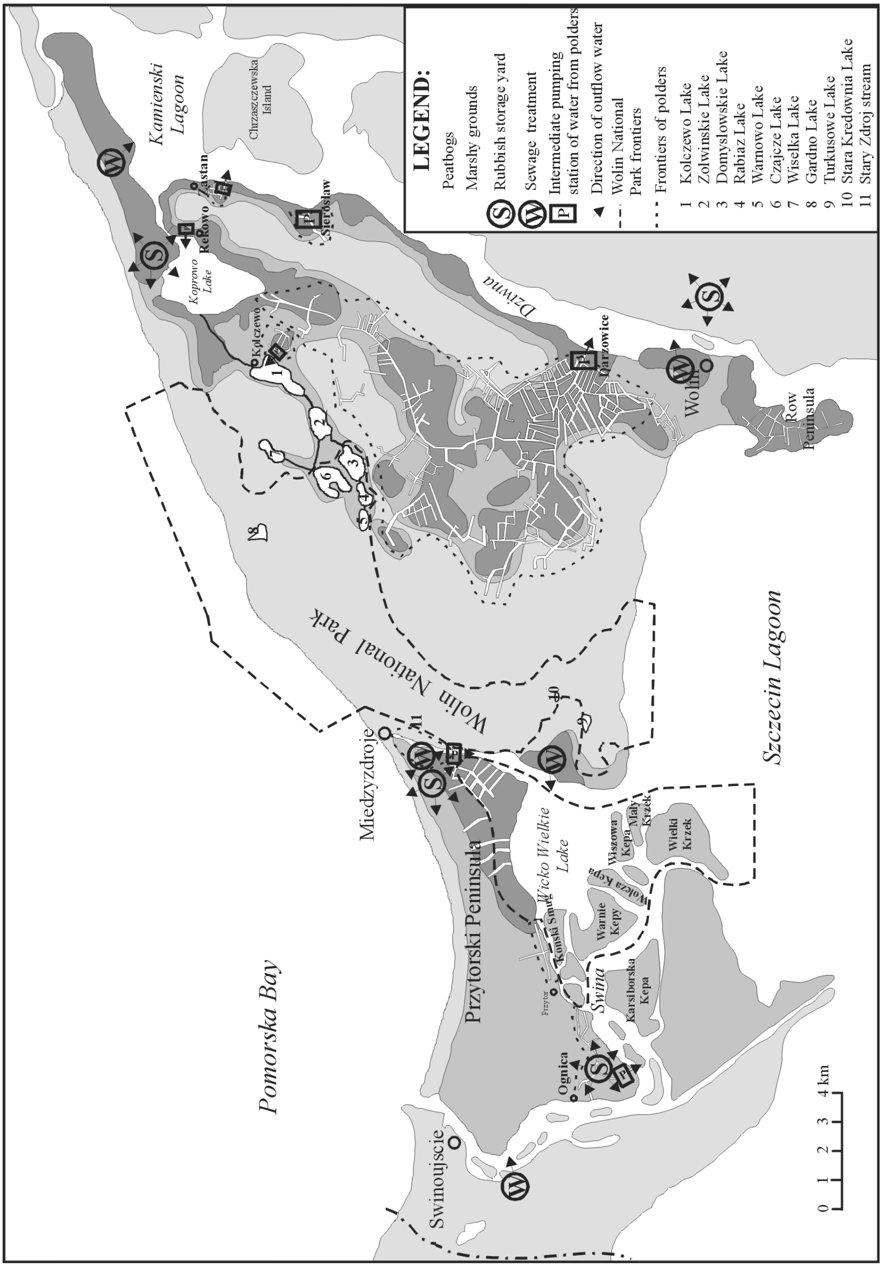

Fig. 1. Wolin Island – water ecosystems [1, 2]

shape of a clinograde, whereas in shallow lakes, frequently polymiction ones, where in fact only epilimnion occurs, the water often stays saturated with oxygen almost to the bottom provided that phytoplankton, most generally, finds good habitat conditions in the body of water [3].

This was also the case as far as water saturation by O_2 during summer stagnation in the Warnowo, Rabiaz, Czajcze and Domyslowskie Lakes in the Wolin National Park (WNP) on the Wolin Island is concerned (*eg* [4]) (Fig. 1 and 2). However, from 2005 onward, clear oxygen deficits in the waters of the aforementioned lakes during summer stagnation being maintained practically constantly were more frequently observed (*eg* [5]).

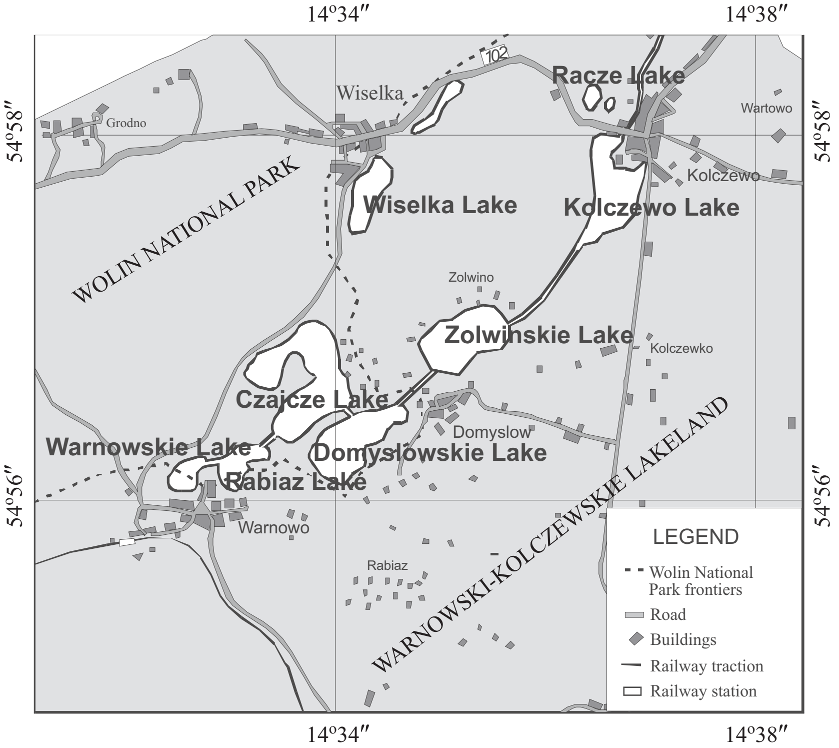

Fig. 2. Warnowo, Rabiaz, Czajcze and Domyslowskie lakes in Wolin National Park [5]

This paper is dedicated to the analysis of the causes of this phenomenon and the attempts to explain them.

Characteristics of the lakes of the Warnowo-Kolczewo Lake District situated within the Wolin National Park

The Warnowo, Rabiaz, Czajcze and Domyslowskie Lakes, situated in the western part of the Warnowo-Kolczewo Lake District within the Wolin National Park, are shallow, ribbon glacial lakes being fed by rain and subsoil waters flowing down from the heights of the Wolin Island. All these lakes, starting from the Warnowo Lake, are connected by narrow inlets the course of which is being presently called the Lewinska Stream (formerly known as the Pojezierna Stream – [6]), rising in the Warnowo Lake and having its mouth in the Kamien Bay. Spring melt waters flow down the Lewinska Stream from the aforementioned lakes successively, starting with the Warnowo Lake, through the Rabiaz and Czajcze Lakes, to the Domyslowskie Lake and further to next lakes of the Warnowo-Kolczewo Lake District on the flow path of the Lewinska Stream water being situated already outside the Wolin National Park. The morphometric characteristics of the lakes under analysis is presented below in Table 1.

Table 1

Morfometric characteristic of lakes: Warnowo, Rabiaz, Czajcze, Domyslowskie [7]

Lake	Altitude [m a.s.l]	Surface [km^2]	Depth [m]		Volume [thousand m^3]	Max. length [m]	Max. width [m]	Cryptodepression [m]
			max.	average				
Warnowo[1]	1.4	0.127	2.1	1.3	160.70	470	411	0.7
Rabiaz[1]	1.4	0.182	2.8	1.5	280.10	654	362	1.4
Czajcze	1.3	0.812	6.0	2.9	2316.70	1520	830	4.7
Domyslowskie	1.3	0.529	3.1	1.9	1018.00	1200	600	1.8

[1] Lakes Warnowo and Rabiaz in the past [6] was called Warnowskie Lake with partitions: Warnowskie Western (now Warnowo) and Warnowskie Eastern (now Rabiaz), or generally warnowskie lakes.

Material and methods

The analyses conducted in arbitrary chosen time periods in summer in 2007, 2008 and 2010 included determination of vertical temperature and oxygen profiles, with measurement of water temperature and dissolved oxygen concentration as well as calculation of water saturation by O_2, at chosen gauging stations on the aforementioned lakes being situated near sink bowls (Fig. 3) down to the depth of 0.5 m above the bottom. Selected water quality parameters of the surface water (0.5 m below the water surface) and the benthic zone (0.5 m above the bottom) were also determined, particularly – apart from water temperature and dissolved oxygen concentration – the redox potential Eh, indices describing the quantity of dissolved organic matter (COD-Mn, COD-Cr and BOD_5), mineral nitrogen concentrations (NO_3^-, NO_2^-, NH_4^+) and N_{tot}, as well as $PO_4^{3-}{}_{dissolved}$ and P_{tot}, and selected indices describing the mineralisation of the investigated waters (concentrations of Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- as total alkalinity, and Fe_{tot} and Mn_{tot}). All determinations were performed based on the analytical procedures currently being in force in the Polish Standards [8], apart from the redox potential Eh which was measured according to the procedure described by Koelling [9].

Also the extent of coverage by macrophytes and floating plants of the surface area of the aforementioned lakes was estimated from the boat's deck.

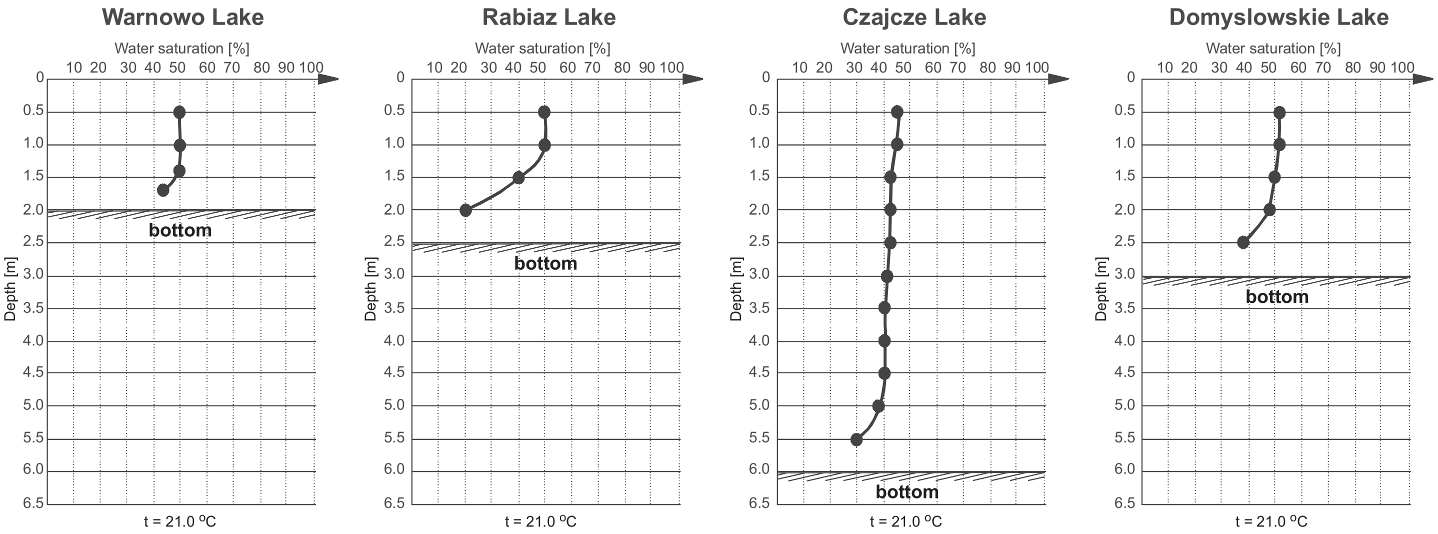

Fig. 3. Water saturation by O_2 of Warnowo, Rabiaz, Czajcze and Domyslowskie lakes in Wolin National Park in vertical profiles in date 30.07.2010

Results and discussion

Selected results of the surface and near-bottom waters of the Warnowo-Kolczewo Lake District lakes in the Wolin National Park are presented in Tables 2–5.

Table 2

Results of researches surfaces and near bottom waters from Warnowo, Rabiaz, Czajcze and Domyslowskie lakes in Wolin National Park (sampling date: 14.09.2007)

No.	Indices	Warnowo Lake		Raciaz Lake		Czajcze Lake		Domyslowskie Lake	
		surface waters	near bottom waters	surface waters	near bottom waters	surface waters	near bottom waters	surface waters	near bottom waters
I. General parameters									
1	Temperature [^{o}C]	17.5	17.4	17.5	17.3	16.0	15.6	16.5	16.3
2	pH [pH units]	7.28	7.18	7.45	7.28	7.34	7.16	7.38	7.12
3	Eh [mV]	402	398	401	376	402	368	402	359
4	COD-Mn [mgO$_2$ · dm^{-3}]	10.2	11.1	10.1	10.0	9.3	9.8	10.0	9.7
5	COD-Cr [mgO$_2$ · dm^{-3}]	38.7	48.6	22.9	37.1	21.5	29.4	30.1	35.6
6	BOD$_5$ [mgO$_2$ · dm^{-3}]	1.4	1.7	1.6	1.4	2.6	2.3	7.9	6.4
7	O$_{2(diss)}$ [mgO$_2$ · dm^{-3}]	4.3	3.7	4.2	3.9	5.8	4.6	9.6	6.7
8	Water saturation by O$_2$ [%]	44.6	38.2	43.6	40.2	58.3	45.8	97.5	67.6
II. Content of biogenic substances									
9	NO$_3^-$ [mgN-NO$_3$ · dm^{-3}]	0.11	0.08	0.08	0.06	0.07	0.05	0.07	0.04
10	NO$_2^-$ [mgN-NO$_2$ · dm^{-3}]	0.14	0.090	0.044	0.023	0.010	0.016	0.007	0.006
11	NH$_4^+$ [mgN-NH$_4$ · dm^{-3}]	0.06	0.14	0.08	0.12	0.03	0.08	0.04	0.07
12	N$_{tot}$ [mgN · dm^{-3}]	0.24	0.49	0.23	0.35	0.19	0.27	0.20	0.15
13	PO$_4{}^{3-}{}_{diss}$ [mgPO$_4$ · dm^{-3}]	0.33	0.37	0.25	0.31	0.36	0.43	0.31	0.51
14	P$_{tot}$ [mgPO$_4$ · dm^{-3}]	0.91	0.59	0.71	0.89	0.44	0.64	0.62	0.78
III. Mineralization indices									
15	Ca^{2+} [mgCa · dm^{-3}]	62	63	54	60	60	64	58	62
16	Mg^{2+} [mgMg · dm^{-3}]	11	14	15	12	12	14	11	15
17	Cl$^-$ [mgCl · dm^{-3}]	20	22	24	28	20	23	24	27
18	SO$_4^{2-}$ [mgSO$_4$ · dm^{-3}]	27	31	16	24	23	26	24	29
19	Total alkalinity [mmol HCl · dm^{-3}]	3.10	3.20	2.70	2.75	3.20	3.30	3.00	3.10
20	Fe$_{tot}$ [mgFe · dm^{-3}]	0.05	0.10	0.05	0.08	0.01	0.10	0.17	0.20
21	Mn$_{tot}$ [mgMn · dm^{-3}]	0.20	0.24	0.15	0.19	0.03	0.10	0.17	0.20

Table 3

Results of researches surfaces and near bottom waters from Warnowo, Rabiaz, Czajcze and Domyslowskie lakes in Wolin National Park (sampling date: 25.06.2008)

No.	Indices	Warnowo Lake		Raciaz Lake		Czajcze Lake		Domyslowskie Lake	
		surface waters	near bottom waters	surface waters	near bottom waters	surface waters	near bottom waters	surface waters	near bottom waters
	I. General parameters								
1	Temperature [^{o}C]	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
2	pH [pH units]	8.07	7.93	7.97	7.54	7.85	7.67	8.01	8.02
3	Eh [mV]	509	498	509	516	492	466	460	455
4	COD-Mn [mgO$_2$ · dm^{-3}]	10.4	11.6	11.2	12.0	9.3	10.6	8.5	10.3
5	COD-Cr [mgO$_2$ · dm^{-3}]	72.0	89.3	52.2	69.9	32.4	43.6	30.6	68.4
6	BOD$_5$ [mgO$_2$ · dm^{-3}]	1.2	1.8	2.5	1.8	1.1	2.9	2.5	0.7
7	O$_{2(diss)}$ [mgO$_2$ · dm^{-3}]	4.2	3.7	4.4	1.8	4.1	2.9	4.6	3.1
8	Water saturation by O$_2$ [%]	46.7	41.2	48.9	20.0	45.6	32.3	51.2	34.5
	II. Content of biogenic substances								
9	NO$_3^-$ [mgN-NO$_3$ · dm^{-3}]	0.06	0.08	0.11	0.07	0.07	0.08	0.07	0.11
10	NO$_2^-$ [mgN-NO$_2$ · dm^{-3}]	0.012	0.020	0.005	0.019	0.010	0.021	0.007	0.010
11	NH$_4^+$ [mgN-NH$_4$ · dm^{-3}]	0.11	0.18	0.18	0.24	0.14	0.20	0.06	0.20
12	N$_{tot}$ [mgN · dm^{-3}]	0.29	0.42	0.47	0.53	0.36	0.49	0.23	0.51
13	PO$_4^{3-}$$_{diss}$ [mgPO$_4$ · dm^{-3}]	0.06	0.15	0.03	0.12	0.20	0.28	0.14	0.15
14	P$_{tot}$ [mgPO$_4$ · dm^{-3}]	0.22	0.29	0.14	0.20	0.25	0.36	0.30	0.28
	III. Mineralization indices								
15	Ca^{2+} [mgCa · dm^{-3}]	84	71	68	70	68	71	68	72
16	Mg^{2+} [mgMg · dm^{-3}]	7	11	12	16	10	14	10	10
17	Cl$^-$ [mgCl · dm^{-3}]	23	25	31	36	21	24	20	20
18	SO$_4^{2-}$ [mgSO$_4$ · dm^{-3}]	51	54	55	59	53	56	54	53
19	Total alkalinity [mmol HCl · dm^{-3}]	3.20	3.20	3.40	3.20	2.80	3.10	3.00	3.00
20	Fe$_{tot}$ [mgFe · dm^{-3}]	0.17	0.20	0.11	0.18	< 0.01	0.10	0.11	0.05
21	Mn$_{tot}$ [mgMn · dm^{-3}]	0.22	0.28	0.21	0.24	0.18	0.22	0.24	0.20

Table 4

Results of researches surfaces and near bottom waters from Warnowo, Rabiaz, Czajcze and Domyslowskie lakes in Wolin National Park (sampling date: 9.08.2008)

No.	Indices	Warnowo Lake		Raciaz Lake		Czajcze Lake		Domyslowskie Lake	
		surface waters	near bottom waters	surface waters	near bottom waters	surface waters	near bottom waters	surface waters	near bottom waters
I. General parameters									
1	Temperature [^{o}C]	23.0	22.9	23.0	22.9	23.0	22.7	23.0	22.9
2	pH [pH units]	8.78	8.65	8.38	7.98	8.44	8.12	8.54	8.14
3	Eh [mV]	398	412	411	435	412	416	407	409
4	COD-Mn [$mgO_2 \cdot dm^{-3}$]	10.5	11.7	10.0	11.9	8.5	10.4	8.5	9.9
5	COD-Cr [$mgO_2 \cdot dm^{-3}$]	182.8	179.3	215.4	198.6	73.4	81.7	39.2	47.6
6	BOD_5 [$mgO_2 \cdot dm^{-3}$]	1.0	1.4	0.6	1.2	2.0	2.3	1.5	1.8
7	$O_{2(diss)}$ [$mgO_2 \cdot dm^{-3}$]	4.3	3.9	3.8	3.1	4.2	3.7	4.6	4.2
8	Water saturation by O_2 [%]	49.5	44.8	43.8	35.6	48.4	42.4	53.0	48.3
II. Content of biogenic substances									
9	NO_3^- [$mgN\text{-}NO_3 \cdot dm^{-3}$]	0.10	0.08	0.15	0.10	0.13	0.09	0.09	0.07
10	NO_2^- [$mgN\text{-}NO_2 \cdot dm^{-3}$]	0.009	0.012	0.013	0.018	0.014	0.016	0.006	0.009
11	NH_4^+ [$mgN\text{-}NH_4 \cdot dm^{-3}$]	0.10	0.18	0.21	0.31	0.19	0.26	0.12	0.19
12	N_{tot} [$mgN \cdot dm^{-3}$]	0.44	0.65	0.54	0.71	0.48	0.59	0.57	0.71
13	$PO_4^{3-}{}_{diss}$ [$mgPO_4 \cdot dm^{-3}$]	0.11	0.16	0.13	0.17	0.06	0.10	0.45	0.51
14	P_{tot} [$mgPO_4 \cdot dm^{-3}$]	0.20	0.25	0.27	0.31	0.43	0.45	0.47	0.53
III. Mineralization indices									
15	Ca^{2+} [$mgCa \cdot dm^{-3}$]	60	58	60	61	84	76	72	63
16	Mg^{2+} [$mgMg \cdot dm^{-3}$]	7	16	10	14	10	12	12	14
17	Cl^- [$mgCl \cdot dm^{-3}$]	25	26	38	40	21	23	20	21
18	SO_4^{2-} [$mgSO_4 \cdot dm^{-3}$]	49	51	74	75	56	60	57	59
19	Total alkalinity [$mmol\ HCl \cdot dm^{-3}$]	3.40	3.50	3.90	4.00	4.00	3.90	4.10	4.00
20	Fe_{tot} [$mgFe \cdot dm^{-3}$]	0.31	0.36	0.27	0.35	0.23	0.28	0.15	0.19
21	Mn_{tot} [$mgMn \cdot dm^{-3}$]	0.37	0.40	0.35	0.38	0.41	0.40	0.34	0.38

Table 5

Results of researches surfaces and near bottom waters from Warnowo, Rabiaz, Czajcze and Domyslowskie lakes in Wolin National Park (sampling date: 30.07.2010)

No.	Indices	Warnowo Lake		Raciaz Lake		Czajcze Lake		Domyslowskie Lake	
		surface waters	near bottom waters	surface waters	near bottom waters	surface waters	near bottom waters	surface waters	near bottom waters
I. General parameters									
1	Temperature [^{o}C]	24.5	22.0	24.0	22.5	23.0	19.0	23.0	24.5
2	pH [pH units]	8.08	8.00	7.58	7.49	7.60	7.62	7.90	7.85
3	Eh [mV]	165	161	165	162	158	210	165	173
4	COD-Mn [mgO$_2$ · dm^{-3}]	10.9	9.9	8.4	9.7	8.0	8.2	8.6	9.0
5	COD-Cr [mgO$_2$ · dm^{-3}]	82.1	79.3	90.1	78.3	62.1	63.7	42.1	43.7
6	BOD$_5$ [mgO$_2$ · dm^{-3}]	1.5	1.8	1.2	1.0	1.5	2.0	1.8	2.1
7	O$_{2(diss)}$ [mgO$_2$ · dm^{-3}]	4.6	4.2	5.0	4.8	4.6	4.3	4.7	4.2
8	Water saturation by O$_2$ [%]	55.0	48.0	58.7	55.0	52.6	46.3	53.7	47.6
II. Content of biogenic substances									
9	NO$_3^-$ [mgN-NO$_3$ · dm^{-3}]	0.13	0.10	0.18	0.16	0.12	0.12	0.18	0.18
10	NO$_2^-$ [mgN-NO$_2$ · dm^{-3}]	0.035	0.020	0.025	0.027	0.014	0.016	0.018	0.020
11	NH$_4^+$ [mgN-NH$_4$ · dm^{-3}]	0.51	0.59	0.32	0.43	0.18	0.22	0.20	0.21
12	N$_{tot}$ [mgN · dm^{-3}]	0.98	0.96	0.74	0.80	0.46	0.49	0.30	0.48
13	PO$_4^{3-}$$_{diss}$ [mgPO$_4$ · dm^{-3}]	0.44	0.60	0.35	0.40	0.50	0.48	0.58	0.61
14	P$_{tot}$ [mgPO$_4$ · dm^{-3}]	0.75	0.91	0.80	0.63	0.59	0.57	0.69	0.73
III. Mineralization indices									
15	Ca^{2+} [mgCa · dm^{-3}]	75	63	69	58	60	62	62	64
16	Mg^{2+} [mgMg · dm^{-3}]	24	18	20	18	18	24	12	28
17	Cl$^-$ [mgCl · dm^{-3}]	18	22	24	26	25	26	23	29
18	SO$_4^{2-}$ [mgSO$_4$ · dm^{-3}]	45	50	55	63	48	88	46	48
19	Total alkalinity [mmol HCl · dm^{-3}]	3.50	3.60	2.50	2.00	3.40	3.50	3.30	3.20
20	Fe$_{tot}$ [mgFe · dm^{-3}]	0.25	0.35	0.35	0.46	0.25	0.26	0.24	0.26
21	Mn$_{tot}$ [mgMn · dm^{-3}]	0.07	0.04	0.07	0.04	0.06	0.08	0.02	0.04

Example water saturation by O_2 profiles are presented in Fig. 3, whereas selected bathymetric cross-sections of the Lewinska Stream within the section between the Warnowo Lake and the Domyslowskie Lake with the distribution of water layers of different water saturation by O_2 being marked on them in the longitudinal cross-section along the water flow path are presented in Fig. 4.

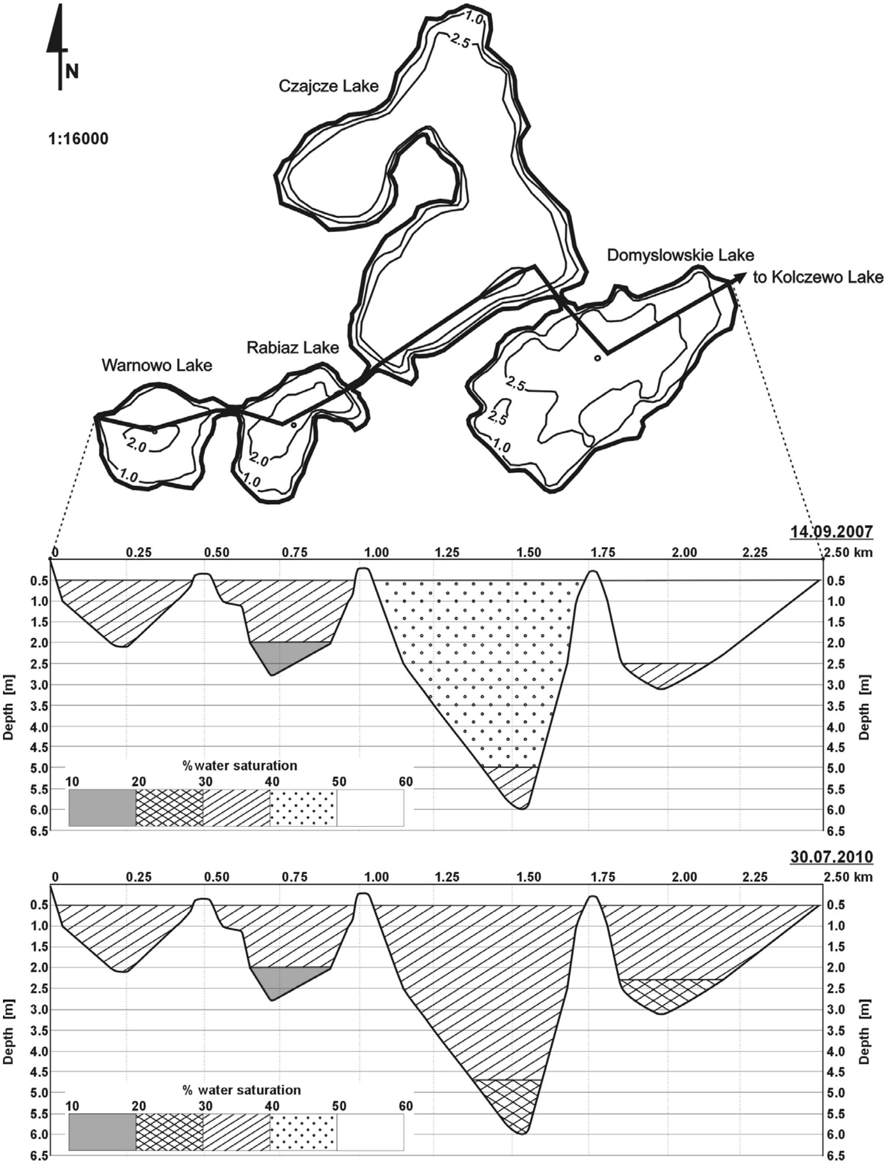

Fig. 4. Bathymetric section of Lewinska Stream on fragment from Warnowo Lake to Domyslowskie Lake with show water layers by different water saturation by O_2

The distribution of rush vegetation and floating plants in the Warnowo lakes being situated within the Wolin National Park in July 2010 is presented in Fig. 5.

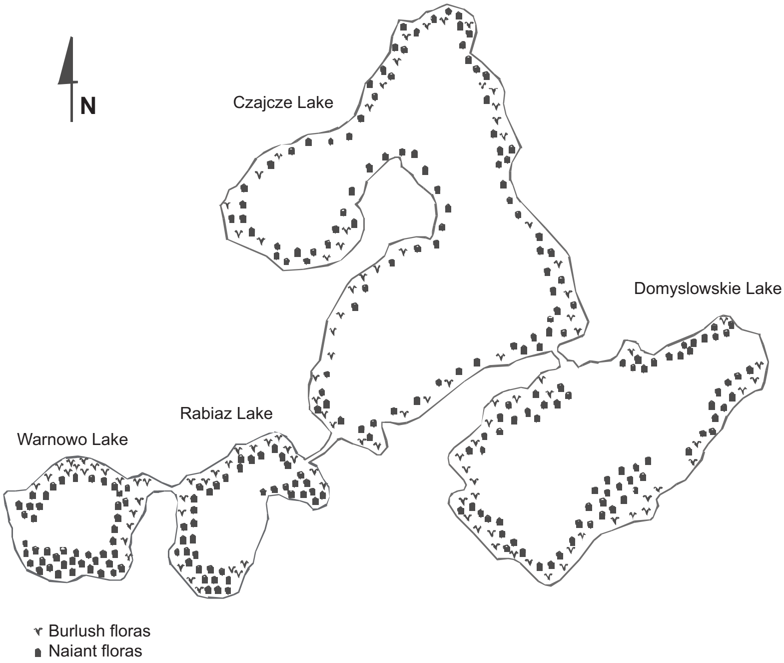

Fig. 5. Collocation bulrush floras and naiant flora in Warnowo, Rabiaz, Czajcze and Domyslowskie lakes in Wolin National Park in second half of July 2010

The collected research data, being illustrated by the results mentioned above, allowed determination that the waters of the Warnowo Lake (average depth 1.6 m) were mostly always practically homothermic and similarly oxygenated (40–45 % water saturation by O_2) in the whole vertical profile, whereas those of the Rabiaz Lake (average depth 1.4 m) – while being homothermic – were characterised by different oxygenation (surface water *ca* 50 % water saturation by O_2, near-bottom water < 20 %). The waters of the Czajcze Lake (average depth 2.9 m) – being also homothermic – were of different water saturation by O_2 on the surface (*ca* 50 %) and the bottom (*ca* 30 %), like those of the Domyslowskie Lake (average depth 2.1 m), also homothermic and with similar water saturation by O_2 like in the Czajcze Lake. At the same time, the waters of the lakes under analysis were characterised by an appreciable content of organic matter which, in consecutive lakes under analysis, was characterised by the COD-Cr values amounting, respectively, to *ca* 50, 50, 30 and 30 $mgO_2 \cdot dm^{-3}$ in the surface water and *ca* 50, 95, 30 and 70 $mg\ O_2 \cdot dm^{-3}$ in the near-bottom one. According to the data from Tables 2–5, the waters under analysis were usually characterised in the measuring times by high values of the redox potential values (on average 400–450 mV), indicating their high oxidative status, and high concentrations of mineral nitrogen and dissolved orthophosphates(V), being considerably higher than nutritional minima for the most requiring alga species [3]. High supply of assimilable nitrogen and phosphorus was most obviously connected with the inflow of biogenic substances from the drainage basin (probably the inflow of effluents with subsoil waters being polluted with municipal sewage discharged to the ground), as well as above all with the processes of organic matter mineralisation taking place in the lake ecosystem. The investigated waters contained small quantities of biodegradable organic matter, which is indicated by low BOD_5 values for the analysed waters amounting maximally to 2.5 $mgO_2 \cdot dm^{-3}$. Differences in water saturation by O_2 in the vertical profiles of consecutive investigated lakes were noteworthy (Table 2–5 and Fig. 4), which is also the proof of slight water exchange between the investigated lakes, being confirmed as well by findings of Burchardt et al [10] from the study carried out in spring 2008 which showed essential differences in dominant species of the phytoplankton of the investigated lakes. And thus, in the Warnowo lakes (*ie* in the Warnowo and Rabiaz Lakes) prevailed *Ochromonas* sp. with a large participation of *Fragilaria pinnata*, *Asterionella formosa* and *Cyclotella radiosa*, in the Czajcze Lake – *Asterionella formosa* and *Fragilaria crotonensis*, whereas in the Domyslowskie Lake – *Limnothrix redeckei*, *Dinobryon bavaricum*, *Fragilaria ulna* and *Fragilaria ulna* var. *angustissima*. This points to the maintenance of water exchange between the Warnowo Lake and the Rabiaz Lake, affecting the phytoplankton phytocenoses, as well as to the limitation of water exchange between the Rabiaz Lake and the Czajcze Lake and further on between the Czajcze Lake and the Domyslowskie Lake, which was confirmed by field observations. This is undoubtedly a consequence of drainage of the eastern part of the Wolin Island by complex drainage system with a drainage water pumping station in Darzowice (Fig. 1), pumping over to 20 m^3/s drainage water to the Dziwna Strait. This induced the lowering of ground water level in the eastern part of the Wolin Island and the lowering of water level in the Warnowo-Kolczewo Lake District lakes by about 0.5 m, considerably affecting this way the functioning of ecosystems of these lakes [11].

The acid-base equilibrium and the content of mineral substances in the waters of analysed lakes were very similar on all water bodies in successive study times. This is obvious given that all water bodies being analysed were “flushed” by the waters flowing down from under the heights in the western part of the Wolin Island during the spring flow of melt waters.

The authors of this paper judge that low water saturation by O_2 in the investigated lakes was a consequence of exuberant growth of plants with floating leaves of the plant community *Nupharo-Nymphaeetum albae* (yellow water-lily and European white water-lily) which, according to the authors’ estimates, occupied approximately 50 % of the area of the water table in each lake. Exceptionally low water saturation by O_2 of the near-bottom water in the Rabiaz Lake was probably a consequence of the flow of anthropogenic pollutants from the village of Warnowo, like in the Domyslowskie Lake being polluted due to vicinity of the village of Domyslow. Both these factors cause that hopes for spontaneous reclamation of water ecosystems of the investigated lakes are illusory. Unfortunately, the “initiation” of oligotrophication processes usually requires artificial interventions [3]. In the opinion of the authors of this paper, leaving the lakes of the Warnowo-Kolczewo Lake District in the Wolin National Park to their own devices would rather induce dystrophication than oligotrophication. Bringing the waters of the Warnowo, Rabiaz, Czajcze and Domyslowskie Lakes to the state of oligotrophy is a task deriving from the Water Framework Directive of the European Union. This is exactly the trophic status of the investigated lakes in the time period prior to increased anthropogenic pressure which is evidenced by the remains of underwater meadows in the Warnowo and Rabiaz Lakes, being still colonised by stoneworts *Chara tomentosa* L. (*eg* [12]).

Conclusions

The occurrence and the maintenance of water homothermy during summer stagnation being found based on the analyses conducted in 2007, 2008 and 2010, particularly specific considerable oxygen deficiency being practically constant in vertical profiles of the waters (from 0.5 m below the water table to 0.5 m above the bottom) of the Warnowo, Rabiaz, Czajcze and Domyslowskie Lakes situated within the Wolin National Park belonging to the Warnowo-Kolczewo Lake District on the Wolin Island was induced by the maintenance and even by the increase of anthropogenic pressure on the ecosystems of the lakes under analysis, being connected with settlement in areas around these lakes, which contributed to the development of dystrophication of the investigated lakes being manifested as exuberant growth of rush vegetation and, first of all, floating plants which significantly reduced surface water aeration and limited the development of water-oxygenating phytoplankton during proliferation of phytoplankton biomass.

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CO SIĘ DZIEJE W WODACH JEZIOR WARNOWO, RABIĄŻ, CZAJCZE I DOMYSŁOWSKIE W WOLIŃSKIM PARKU NARODOWYM PODCZAS STAGNACJI LETNICH?

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Abstrakt: W latach 2007, 2008 i 2010 w okresach letnich wyznaczano profile temperaturowe i natlenienia wód w połączonych ze sobą przesmykami jeziorach Warnowo, Rabiąż, Czajcze i Domysłowskie leżących w granicach Wolińskiego Parku Narodowego na wyspie Wolin na Pojezierzu Warnowsko-Kołczewskim. Wykazano występowanie homotermii i praktycznie stałego natlenienia wód od 0.5 m od powierzchni do 0.5 m powyżej dna, przy czym badane wody cechowały się zdecydowanym niedotlenieniem, które było jednakże w kolejnych jeziorach zróżnicowane. Wyniki oznaczeń wskaźników ogólnych, stężeń biogenów i wskaźników mineralizacji, wskazywały także na niewielkie, niemniej wyraźne zróżnicowanie chemizmu badanych jezior, co było związane ze zróżnicowaniem antropopresji na poszczególne ekosystemy oraz z ograniczeniem przepływu wód przez kolejne ww. jeziora w dół zlewni. Wskazano, że występowanie niskiego natlenienia wód w toni wodnej badanych jezior związane było z postępującą dystrofizacją badanych ekosystemów jeziornych, uwidaczniającą się jako bujny rozwój roślinności szuwarowej i przede wszystkim roślinności pływającej.

Słowa klucze: jeziora; natlenienie wód; jeziora: Warnowo, Rabiąż, Czajcze i Domysłowskie; Woliński Park Narodowy

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EFFECT OF FERTILISATION WITH NITROGEN MACROELEMENTS ON THE CONTENT OF SULPHUR AND THE ACTIVITY OF ARYLSULPHATASE IN SOIL

WPŁYW NAWOŻENIA MIKROSKŁADNIKAMI NA ZAWARTOŚĆ SIARKI ORAZ AKTYWNOŚĆ ARYLOSULFATAZY W GLEBIE

Abstract: The aim of the present research was to determine the effect of mineral fertilisation only on the activity of arylsulphatase (EC 3.1.6.1.) and the content of total sulphur and its fraction in soil under winter wheat. The soil was sampled from a field experiment set up on the area of the Agricultural Experiment Station at Grabow on the Vistula by the Institute of Soil Science and Plant Cultivation (IUNG) in Pulawy twice in the vegetation period of winter wheat in 2008. The experiment involved only mineral fertilisation: increasing rates of ammonium nitrate (0, 40, 80, 120, 160 kgN $\cdot$ ha^{-1}) and fertilisation with P – 70 kgP$_2$O$_5$ $\cdot$ ha^{-1}, K – 90 kgP$_2$O$_5$ $\cdot$ ha^{-1}, Ca – 200 kgCaO $\cdot$ ha^{-1}, Mg – 70 kgMgO $\cdot$ ha^{-1} and S in fertilisation forms with other elements. The activity of arylsulphatase was determined following the Tabatabai and Bremner method, and sulphate sulphur – compliant with the Bardsley–Lancaster method modified by COMN-IUNG. The fertilisation with ammonium nitrate determined the content of total sulphur and its fraction as well as the activity of arylsulphatase in Luvisol. The optimum nitrogen rate for the application of which the soil was identified with the highest content of total and organic sulphur was the rate of 80 kgN $\cdot$ ha^{-1}. The Luvisol investigated demonstrated a low richness with sulphur and it should be enriched with that nutrient to facilitate the plants producing the yield adequate in both the quality and the size. A decrease in the activity of arylsulphatase when exposed to complete fertilisation with nutrients in a form of mineral salts points to an inactivating effect of ions of those elements on the activity of the enzyme in the soil.

Keywords: arylsulphatase activity, sulphur, soils, makroelements

In the early 1980s numerous ecological actions were taken to reduce the emissions of sulphur compounds to the atmosphere. As a result of its decreased supply from the air accompanied by a limited consumption of sulphur-containing fertilisers there were observed deficits of that element in field crops, *eg* in Great Britain, Germany and Denmark [1–3]. Similarly in Polish agriculture there occur symptoms which point to

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sulphur deficits [4–6]. There is a risk that the NPK fertilisation applied will not be balanced and that sulphur deficit can limit the use of the other nutrients, mostly nitrogen. The metabolism of those elements is interconnected and the deficit of one of them inhibits the effect of the other. An insufficient nutrition of plants with sulphur is seen in the plant look, similarly as when exposed to nitrogen deficit [7]. The difference in the comparison to the nitrogen deficit symptoms is that with nitrogen deficit older leaves get lighter in colour and yellow initially and when exposed to sulphur deficit – those are young leaves which yellow. In such plants there are found considerable amounts of nitrogen in a non-protein form, the content of reducing sugars decreases and the content of starch and hemicelullose increases [3].

The aim of the present paper was to determine the effect of exclusively mineral fertilisation with nitrogen, potassium, phosphorus, calcium, magnesium and sulphur on the content of total sulphur and its fractions as well as the activity of arylsulphatase (EC 3.1.6.1.) in the soil under winter wheat.

Material and methods

The soil was sampled from a field experiment set up at the Agricultural Experiment Station at Grabów nad Wisłą, by the Institute of Soil Science and Plant Cultivation (IUNG) in Puławy twice in the vegetation period of winter wheat in 2008. The soil is a very good rye complex soil. The experiment involved only mineral fertilisation: increasing rates of ammonium nitrate (0, 40, 80, 120, 160 kgN $\cdot$ ha^{-1}) and fertilisation with P – 70 kgP_2O_5 $\cdot$ ha^{-1}, K – 90 kgP_2O_5 $\cdot$ ha^{-1}, Ca – 200 kgCaO $\cdot$ ha^{-1}, Mg – 70 kgMgO $\cdot$ ha^{-1} and S in fertilisation forms with other elements. The experiment was performed as a split-plot design, the first factor involved increasing rates of nitrogen fertiliser, the second factor – fertilisation with the other macroelements. There were applied six levels of the second factor; the first level involved a fertiliser combination of all the minerals and then one of them was absent in each, respectively; hence the following six treatments:

1. P, K, Ca, Mg, S;
2. –, K, Ca, Mg, S;
3. P, –, Ca, Mg, S;
4. P, K, –, Mg, S;
5. P, K, Ca, –, S;
6. P, K, Ca, Mg, –.

Mineral fertilisation was applied only. In the treatments with S there was used single superphosphate and potassium sulphate, while the treatments without S involved triple superphosphate and high-percentage potassium salt.

The activity of arylsulphatase was determined following the Tabatabai and Bremner method [8], and sulphate sulphur – according to the Bardsley–Lancaster method modified by COMN-IUNG [9]. Organic sulphur was calculated from the difference between the content of total sulphur and S-SO_4^{2-}. For the results of the content of sulphur and the activity of the enzyme, there was performed the analysis of variance with the Tuke'y semi-intervals of confidence ($p = 0.05$).

Results and discussion

The reaction of the soil ranged from 6.37 to 6.84 units for the soil sampled from soil from soil was sampled from a field experiment at Grabów nad Wisłą (Table 1). The reaction of the soils analysed ranged from slightly acid through acid to neutral.

Table 1

Reaction (pH in 1mol KCl · dm^{-3}) of soil the years of investigation

Treatments	Nitrogen fertilization [kg · ha^{-1}]				
	0	40	80	120	160
1. P, K, Ca, Mg, S	6.78	6.77	6.68	6.84	6.62
2. –, K, Ca, Mg, S	6.81	6.76	6.65	6.68	6.65
3. P, –, Ca, Mg, S	6.69	6.63	6.69	6.77	6.58
4. P, K, –, Mg, S	6.67	6.84	6.63	6.65	6.54
5. P, K, Ca, –, S	6.72	6.77	6.61	6.64	6.56
6. P, K, Ca, Mg, –	6.56	6.49	6.42	6.63	6.37

The content of total sulphur in the Luvisol investigated was, on average, for all the experimental treatments 0.05 g · kg^{-1}. The range of occurrence of that element in the soil was quite wide and ranged from 0.015 g · kg^{-1} to 0.103 g · kg^{-1} (Fig. 1a, b). The contents of sulphur recorded in the present research classified the soil, applying the grading scale developed by IUNG, as showing a natural ($\leq$ 0.150 g · kg^{-1}) sulphur content [5, 10].

There was observed an effect of the mineral fertilisation applied on the concentration of that nutrient in the soil analysed. The highest contents of total and organic sulphur were determined in the soil sampled from the plots where complete fertilisation with all the macroelements was applied, where the content of S_{tot} was, on average, 0.066 g · kg^{-1} and S_{org} 59.00 mg · kg^{-1} (Fig. 1b, 2b). The lowest amounts of total sulphur and organic sulphur compounds in the soil, on the other hand, were determined for the treatments with sulphur fertilisation, however, without Ca and Mg fertilisation (Fig. 1b, 2b).

Total sulphur covers a total content of organic and mineral compounds of that element which occurs in soil. In Polish soils organic sulphur is a dominant form of occurrence of that element and its content ranges a lot from 6 to 688 mg · kg^{-1} [5]. The share of that sulphur fraction in total sulphur in the humus horizons of mineral soils accounts for 50–80 % [3]. Liming enhances the release of sulphur *eg* by accelerating the decomposition of organic compounds, leading to the transformation of sulphur into soluble sulphates [9]. Earlier Williams [12] found that the application of $CaCO_3$ results in an increase in the concentration of soluble sulphates and sulphur mineralization up to the value of pH 7.5, above that pH value there occurs a fast process of chemical bonding of sulphates.

The transformations of organic sulphur to the mineral form do not always result in a considerable increase in the content of sulphates in soil [13]. Most probably considerable amounts of inorganic sulphur are leached deep down the soil profile in winter and at the beginning of the vegetation period, especially in light soils [7, 15].

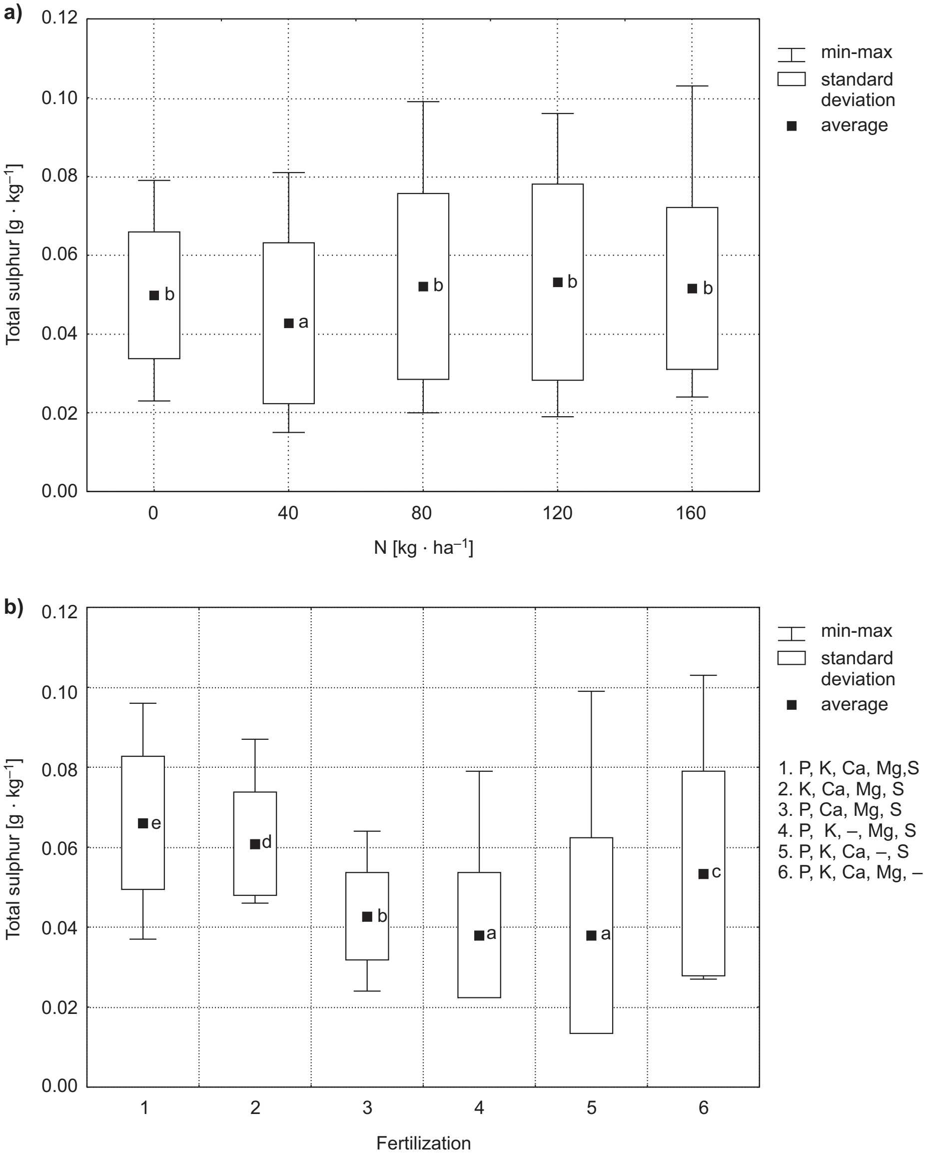

Fig. 1. Content of total sulphur in soil as dependent on fertilization

The fertilisation with ammonium nitrate also modified the content of both sulphur forms. Their lowest amount was reported in the soil sampled from the treatments with the rate of N 40 kgN · ha^{-1} (Fig. 2a, 3a).

The content of the sulphur form available to plants ranged from 2.368 g · kg^{-1} to 14.42 g · kg^{-1} (Fig. 3a, b). In most soils under agricultural use the content of sulphate sulphur in Poland does not exceed 25 mg · kg^{-1} of soil. In most soils, namely

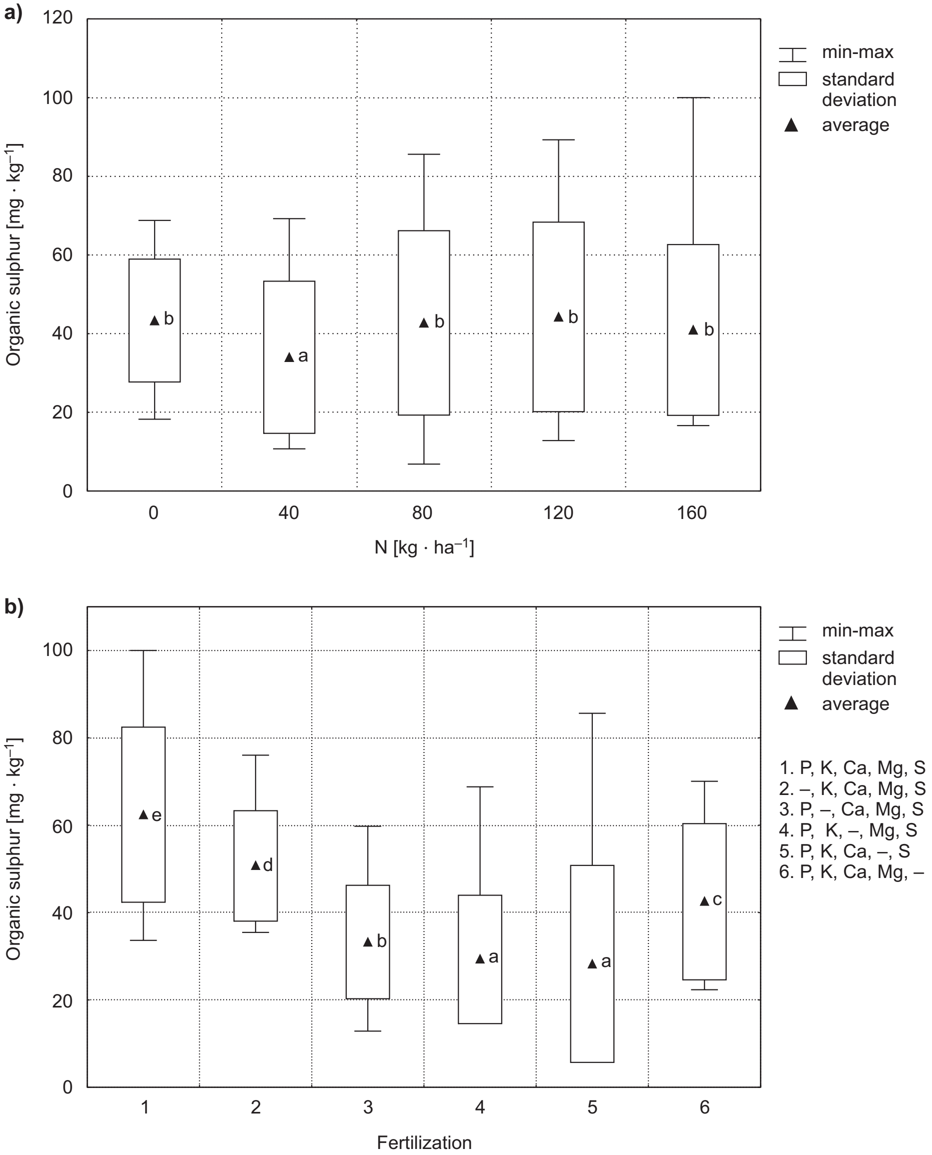

Fig. 2. Content of organic sulphur in soil as dependent on fertilization

70 % of the agricultural acreage, the content of that sulphur fraction ranges from 5.0 to 20.0 mg · kg^{-1} [14]. The content of sulphate sulphur was, on average, 8.219 mg · kg^{-1}. Such soil richness with available sulphur is considered low and wheat, although found to represent the group of plants of low sulphur requirements, needs supplementary sulphur fertilisation [15]. There was noted an effect of the mineral fertilisation applied on the content of that sulphur fraction in the soil from Grabow. The highest content of

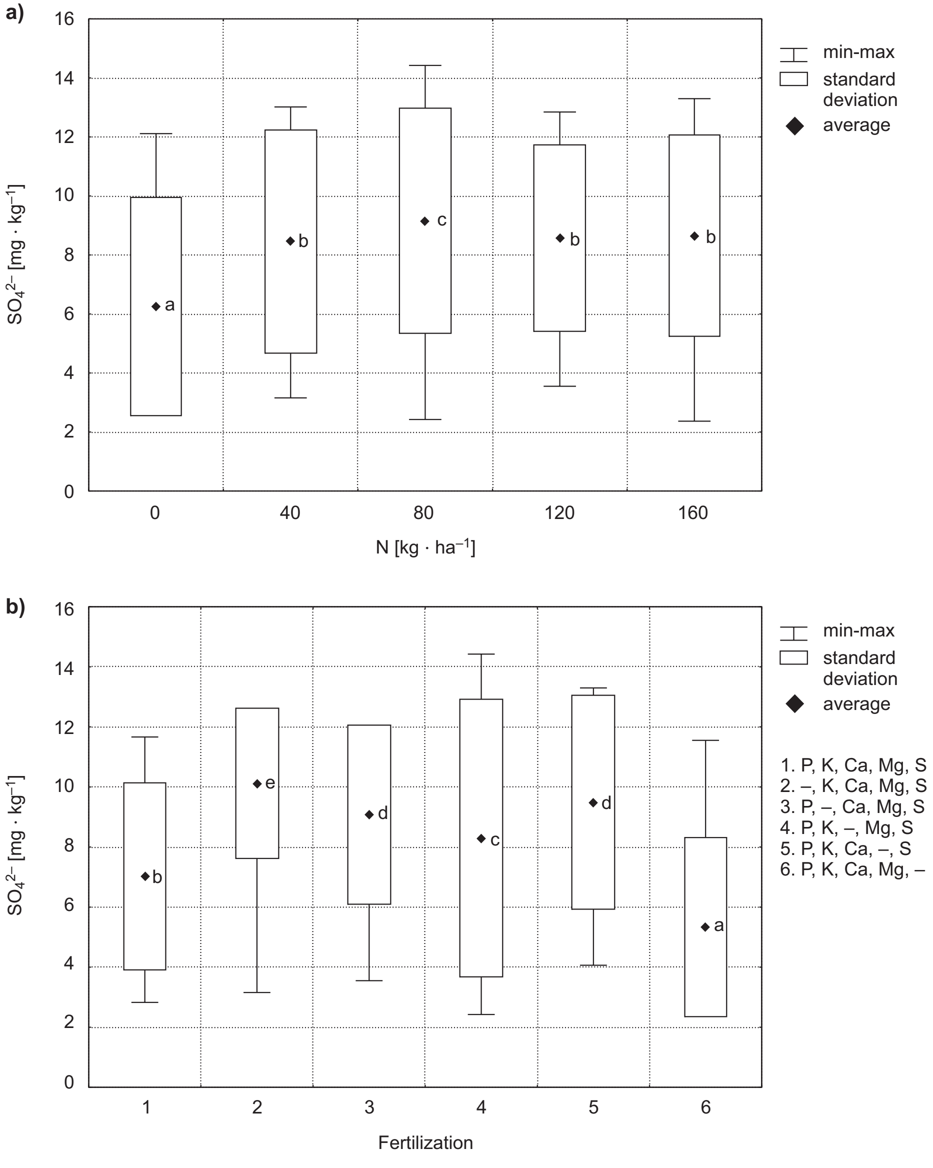

Fig. 3. Content of sulphate sulphur(VI) in soil as dependent on fertilization

sulphate sulphur was recorded in the soil sampled from the treatments with nitrogen fertilisation at the rate of 80 kg · ha^{-1} (Fig. 3a).

The increase in the nitrogen rate to 120 and 160 kg · ha^{-1} resulted in a decrease in the content of the sulphur form available to plants. There was observed an effect of fertilisation with the other macronutrients on the content of S-SO_4^{2-}. The highest content of sulphur available to plants was noted in the soil sampled from the treatments

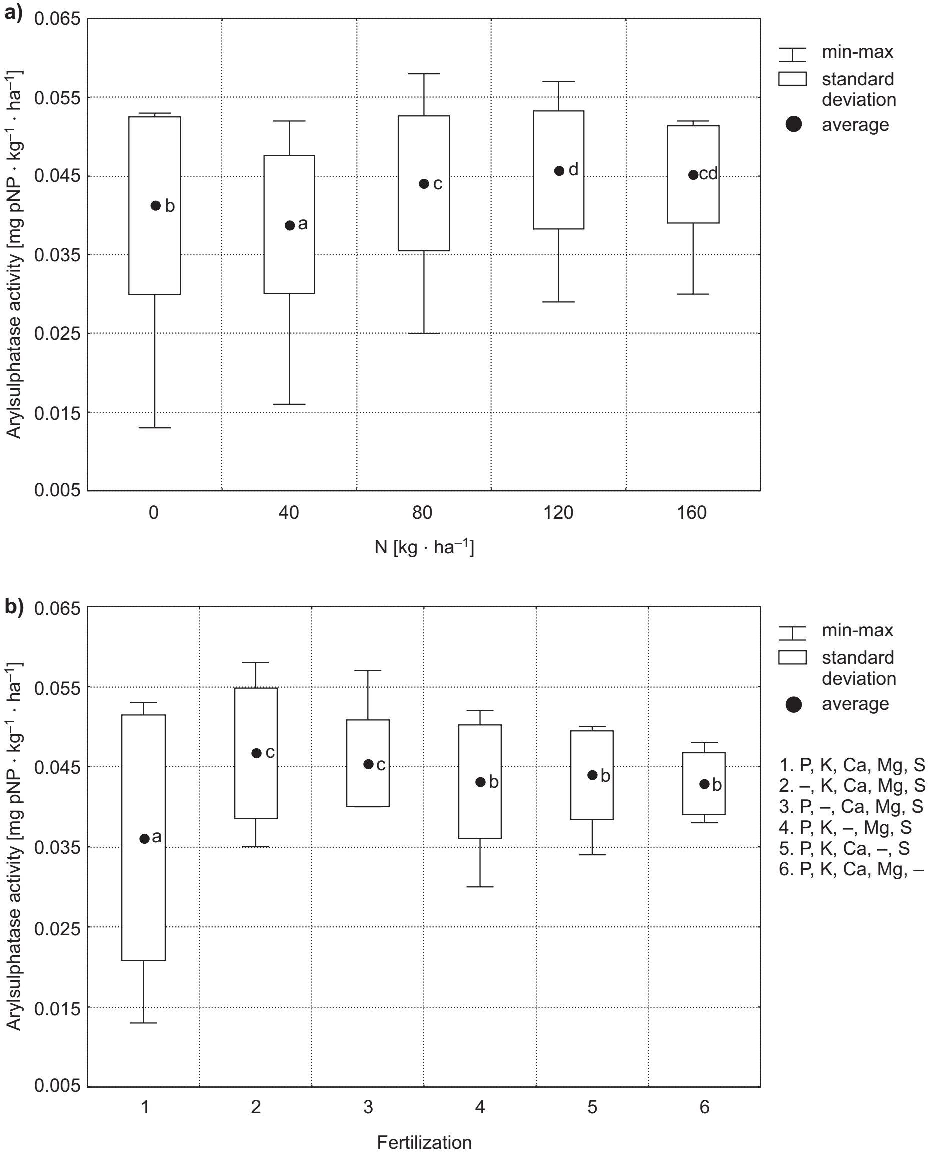

Fig. 4. Arylsulphatase activity in soil as dependent on fertilization

without P fertilisation (treatment 2), a slightly lower – for the treatments without K and Ca (treatments 3 and 5) (Fig. 3b). The lowest amount of S-SO_4^{2-}, on the other hand, was obviously reported in the soil where no fertilisation with that nutrient was used (Fig. 3b).

There was observed an effect of the mineral fertilisation on the activity of arylsulphatase (Fig. 4a, b). The activity of the hydrolase investigated in the soil sampled from the plots fertilised with nitrogen at the rate of 120 kg · ha^{-1} was highest, while its lowest activity was noted in the soil sampled from the treatments fertilised with ammonium nitrate at the rate of 40 kg · ha^{-1}. As for the control treatment, the activity of hydrolase was 5 % higher. One can thus assume that there must have occurred an inhibition of the activity of that enzyme. The applicable literature [16, 17] reports on a negative effect of ions (NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Cl^-) on the enzymatic activity of soil. The present research also report on an inhibiting effect of mineral salts on the activity of arylsulphatase. Its lowest activity was assayed in the soil sampled from the treatments with complete mineral fertilisation.

Conclusions

1. The fertilisation with ammonium nitrate determined the content of total sulphur and its fraction in Luvisol. The optimum rate of nitrogen in a form of mineral salt was the rate of 80 kg N · ha^{-1}. Higher amounts of that macroelement introduced into soil did not result in an increase in the content of sulphur and its fraction in soil.
2. Complete balanced fertilisation with nitrogen, phosphorus, potassium, magnesium, calcium and sulphur created favourable soil conditions to the occurrence of sulphur of organic compounds and total sulphur in soil.
3. The highest amount of sulphate sulphur (VI) was noted in the soil samples fertilised with potassium, magnesium, calcium and sulphur, however, non-fertilised with phosphorus.
4. The Luvisol investigated showed a low richness with sulphur and, as such, it should be enriched with that nutrient to make it possible for the plants to produce the yield adequate in both the quality and the size.
5. A decrease in the activity of arylsulphatase when exposed to complete fertilisation with nutrients in a form of mineral salts points to an inactivating effect of the ions of those elements on the activity of arylsulphatase in soil.

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WPŁYW NAWOŻENIA MIKROSKŁADNIKAMI NA ZAWARTOŚĆ SIARKI ORAZ AKTYWNOŚĆ ARYLOSULFATAZY W GLEBIE

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Abstrakt: Celem pracy było określenie wpływu wyłącznie mineralnego nawożenia na aktywność arylosulfatazy (EC 3.1.6.1.) oraz zawartość siarki ogółem i jej frakcji w glebie spod uprawy pszenicy ozimej. Próbki gleby pobrano z doświadczenia polowego założonego na terenie RZD w Grabowie nad Wisłą, przez IUNG w Puławach dwukrotnie w sezonie wegetacyjnym pszenicy ozimej w 2008 r. W doświadczeniu zastosowano tylko nawożenie mineralne: wzrastające dawki saletry amonowej (0, 40, 80, 120, 160 kgN $\cdot$ ha^{-1}) oraz nawożenie P – 70 kgP_2O_5 $\cdot$ ha^{-1}, K – 90 kg P_2O_5 $\cdot$ ha^{-1}, Ca – 200 kgCaO $\cdot$ ha^{-1}, Mg – 70 kg MgO $\cdot$ ha^{-1} i S w formach nawozowych z innymi pierwiastkami. Aktywność arylosulfatazy oznaczono wg metody Tabatabai i Bremnera, a siarkę siarczanową zgodnie z metodą Bardsleya–Lancastera w modyfikacji COMN-IUNG. Nawożenie saletrą amonową determinowało zawartość siarki ogółem i jej frakcji oraz aktywność arylosulphatazy w płowej glebie. Optymalną dawką azotu, przy zastosowaniu której stwierdzono w glebie największą ilość siarki ogółem i organicznej, była ilość 80 kgN $\cdot$ ha^{-1}. Badana gleba płowa wykazywała niską zasobność w siarkę i powinna być wzbogacona w ten składnik, by umożliwić roślin wydanie plonu o odpowiedniej jakości i ilości. Zmniejszenie aktywności arylosulfatazy przy pełnym nawożeniu składnikami pokarmowymi w postaci soli mineralnych wskazuje na inaktywujący wpływ jonów tych pierwiastków na aktywność enzymu w badanej glebie

Słowa kluczowe: arylosulphataza, siarka, gleba, makroskładniki

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SUSPENDED PARTICULATE MATTER AS AN INDICATOR OF METALS POLLUTION IN RIVERIN SYSTEM

CHARAKTERYSTYKA ZAWIESINY JAKO WSKAŹNIKA ZANIECZYSZCZENIA ANTROPOGENNEGO METALAMI SYSTEMÓW RZECZNYCH

Abstract: Content of heavy metals is strongly dependent on the composition of suspendend particulate matter (SPM). Metals contamination of the aquatic environment can be natural origin as well as is a result of human activities. SPM is an important indicator of processes occurring in the basin. Mineralogical and geochemical identification and determination of the origin of the suspension components is necessary to evaluate the role of SPM in the accumulation and transport of trace metals in Odra river. Research were carried in the Upper and the Middle Odra River and its tributaries. SPM samples were analyzed with SEM-EDS application and metals in water and SPM were determined by ICP-MS. Result of SEM-EDS shows the presence of carbonates – mainly calcite, silicates – especially quartz and feldspars as well as illit. Obtained results allowed to recognize a variety of plankton species. It should be noted that very common in SPM feldspar and quartz contain relatively low amount of metal, as opposed to clay minerals that are responsible for the pollution. In SPM samples the presence of significant quantities of anthropogenic dust were recognized. Observed metal pollution of the Odra river basin is dangerous because of their toxic nature and the threat to living organisms. Suspended matter seems to be one of the best indicator of antropogenic pollution in riverin system.

Keywords: suspended particulate matter (SPM), heavy metals in Odra river

Trace metals are present in aqueous systems in the form of soluble, colloidal and associated with the solid phase – *suspended particulate matter* (SPM) and river sediment. Clear identification of the SPM transport in the river system is very complex and requires accurate diagnosis of lithological and geochemical basins and a detailed assessment of its impact on the course of chemical reactions in the rivers [1–4]. Quality and quantity of SPM depending on the shape and geology of the river bed (riverbed erosion), of the catchment area (surface denudation) as well as the climate and seasons [5]. In order to determine the degree of contamination by heavy metals of anthropogenic

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origin it should be taken into account geochemical background and suggested the adoption of geochemical background values for clay rocks (similar to SPM mineralogical and chemical composition and physical properties) determined by Turekian and Wedephola [6]. In the SPM similar to sediment – metals accumulate in the finest fraction mainly constructed of clay mineral, iron oxides and manganese and organic matter. Detailed research of heavy metals sources of in river suspended matter are presented by Jedwab [7–8] and Van Maledern et al [9]. Jambers et al [10] determined the high content of organic matter in a particle-rich in Mn, Cr, Zn, Ni. The strong correlation between organic matter and particles rich in heavy metals proves its sorption capacity. These studies have shown the presence of high content of kaolinite in the spring and increased the content of chlorite and biotite during the rainy season. In the spring time the amount of organic matter increasing few times. It is important to mentioned that aluminosilicates can be coated with organic and then be recognized as organic matter. Organic matter can play an important role in the formation and aggregation of minerals [10]. It also confirms that the amount of organic matter in the spring is much higher and variable and the total amount of the SPM during the year is relatively constant. The objectives of this preliminary study were to identify mineralogical and geochemical composition of the suspended matter in the Odra River. Furthermore, discus mobility and potential bioavailability of metals in comparison with the total amount. The Odra River catchment area is 136 528 km^2. In total, there are about 1700 sources of pollutions at the Odra River catchment area, out of which 700 significantly influence the conditions of river system. In the past, in the catchment area of the upper and middle Odra exploited large amounts of iron ore, copper, uranium, arsenic and minor amounts of gold and pyrite. Currently in operation are turoszowskie lignite, copper ore and clays, carbonates and natural aggregates and rock materials, fluorite, barite, gypsum and anhydrite deposits, and having only metallogenic importance of chromium, copper, arsenic, gold, tin, cobalt, nickel and other metals ore. The geological structure, industrial and agricultural activity and localisation of main industrial centers, which are: mining (coal, copper), metallurgy (non-ferrous), electroplating plants, production of dyes, pigments production, pesticides, anticorrosive materials and power industry caused many environmental problems in the Odra Catchment Area. There are many publications about the effect of mining and processing industry on environment in Poland [11–14]. Information on total concentration of metals in SPM is not sufficient to assess their potential toxicity, which depend on their chemical forms [15–16]. Metal speciation are widely used to determined different forms of metals in river system [17–18]. Nevertheless, chemical extraction procedures have been applied mostly on sediments but rarely on SPM. All presented results are supposed to confirm that metals and their forms in suspended particulate matter seems to be be one of the best indicator of antropogenical pollution in riverin system.

Sampling and methods

Research were carried in the Upper and the Middle Odra River. In order to identify the composition of SPM in Chalupki, Scinawa nad Bytom Odrzanski samples of SPM were taken in June 2000 and were analyzed with SEM-EDS application. For the sampling of SPM-samples water from a depth of about 1m was taken to PE-bottles and PE-barrels. After sedimentation a part of the cleared water were decanted. Concentrated suspended matter were filtrater (membrane filter d = 0.45 μm) and freeze dried. Furthermore this material were used for mineralogical and geochemical analyses. The SEM-EDS (HITACHI S-4200 VOYAGER acceleration voltage: 15 keV) was used for preliminary analysis. Samples were dusted with carbon before observation. SEM-EDS analysis were used for identification of individual mineral grains, plankton species and for qualitative information about SPM samples. Detection is possible at certain points.

Results and discussion

SEM results show the presence of carbonates, mainly calcite, silicates – especially quartz and feldspar, illit (Fig. 1).

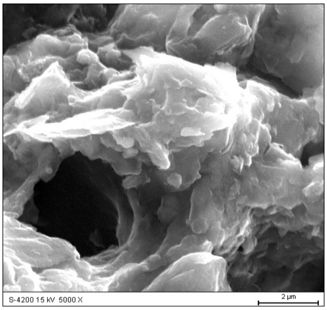

Fig. 1. SEM photo – Illit Chalupki

It should be noted that very common in SPM feldspar (Fig. 2) and quartz (Fig. 3) contain relatively low amount of metal, as opposed to clay minerals that are responsible for the pollution. Fine fraction is composed mainly of silicates, including ilit, smectite and other clay minerals.

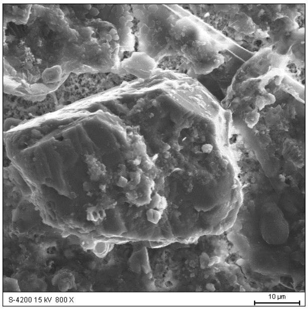

Fig. 2. SEM photo – Feldspar Bytom Odrzanski

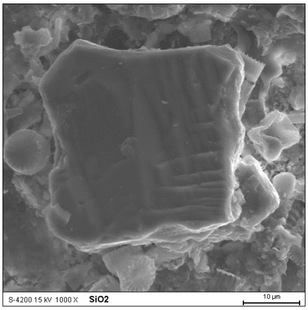

Fig. 3. SEM photo – Quartz – Bytom Odrzanski [19]

Obtained microscopic analyses results allowed to recognize a variety of plankton species, the most common are *Navicula lancelot* (Fig. 4), *Cyclotella meneghiniana* and *Nitzschia acicularis* (Fig. 5). Among others are *Asterionella formosa*, *Aulacoseira granulata*, *Cyclotella radiosa*, *Cymbella silesiaca*, *Diatoma vulgaris*, *Melosira varians*, *Meridion circulare*, *Navicula cryptocephala*, *Nitzschia dubia.*

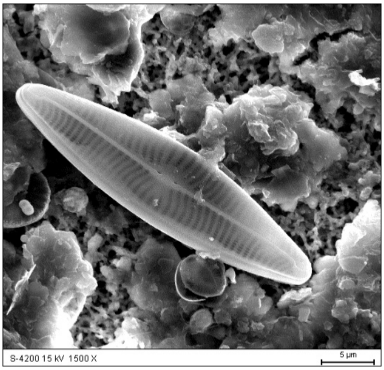

Fig. 4. SEM photo – *Navicula lanceolata* – Chalupki

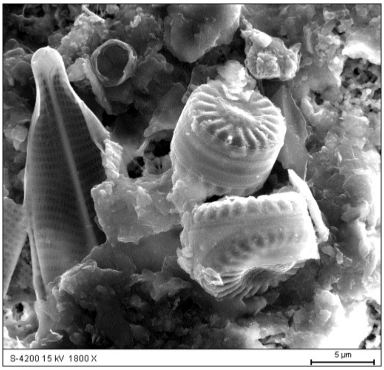

Fig. 5. SEM photo – *Cyclotella meneghiniana*, *Nitzschia acicularis* – Scinawa

In SPM samples the presence of large quantities of anthropogenic dust and grain were recognized (Fig. 6, 7).

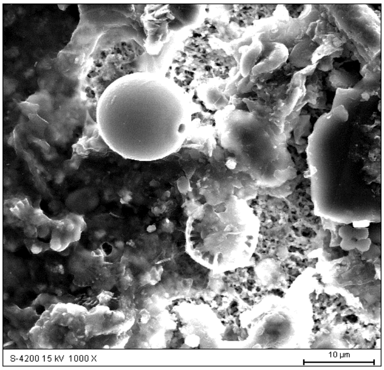

Fig. 6. SEM photo – Antropogenical fly ash – Chalupki [19]

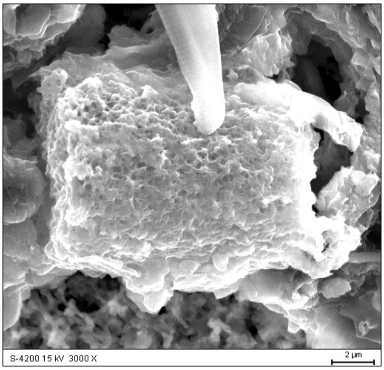

Fig. 7. SEM photo – Aluminosilicate Mn-Ca Anthropogenical origin [19]

Additionally Ca, K and Mg studies were carried out. Obtained concentrations were respectively (average amount mg/dm^3) 71.5, 8.77, 18, 37. In meantime author carried out the detailed study of the amount of SPM and metal content in water and SPM. Over 150 samples of water and SPM were taken from Chalupki to Krosno Odrzanskie during 5 sampling Campaigns from November 1997 to June 2000. Concentration of suspended matter varied significantly from 0.88 to 115.8 mg/kg. Studies showed that Odra River was significantly polluted with Cd and Zn and moderately with other heavy metals (Pb, Ni, Cr, Fe, Cu, Mn) and As, both in the case of water and SPM. Highest Cd, Cu and Zn concentration in water were observed in the middle Odra River. Average concentrations for Cd, Pb, Cu, Zn and As in riverin water were respectively (μg/dm^3) 0.14, 1.77, 8.24, 55.4 and 2.33. Metal contents in SPM varied in wide ranges (mg/kg): 8.0–302 As, 1.75–39.8 Cd, 24.4–401 Pb, 22.1–1287 Ni, 42.4–351 Cr, 6.2–399 Cu, 351–31369 Zn, 1152–11010 Mn and 23881–121316 Fe. Above results and discussion are presented in [19–20]. In case of Cd, Zn, Cu the detected levels of metals in both water and SPM exceeded LAWA targets value [21]. The enrichment factor calculated according to the background values proposed by Turekian and Wedephol [6] and by Martin and Maybeck [3] for As, are as follow: 28.4 (Cd) > 22.8 (Zn) > 11.2 (As) > 8.4 (Pb) > 2.2 (Cu) > 1.5 (Ni) > 1.3 (Cr), [21].

Observed metal pollution of the Odra river basin is dangerous because of their toxic nature and the threat to living organisms. Suspended matter accumulates metals mainly in the fine fraction – clay minerals, iron and manganese oxides and organic matter. In order to determine the metals mobility and the different forms of metal binding in the suspension sequential extraction procedure was applied. In June 2000 – 9 SPM samples from river and 6 from tributaries were taken in order to estimate the mobility and potential bioavailability of metals in SPM. Detailed results were published in [19]. After selective chemical extractions procedure according to Calmano [22] metals were analyzed by ICP-MS. In order to estimate accuracy of the analytical method, reagent blanks and certified reference materials (riverine water 1643d, Lake Sediment LSKD-4) were used to assure criteria related to quality of the analytical results. Unambiguously of ICP-MS technique was confirmed by TXRF.

Considering the mobility of metals in the suspended matter, the exchangeable and bound with carbonates, easily and moderately reducible, sulfidic and organic as well as metal in residuum were estimated using the sequential extraction procedure. Results show that about 25 % of As is bounded to carbonates. As is mainly associated with Mn oxides (60 %). Cadmium is easily exchangeable and associated with carbonates and Mn oxides. Most Pb associated with sulfides, organic substances and / or in residum. Zinc is bounded in the first two extraction steps respectively; 24 % and 18 % of Zn in the Odra River and its tributaries is exchangeable and carbonates associated up to 26 % and 14 % respectively in the tributaries of the Oder river. Other quantities mainly in the presence of organic substances and/or sulfides of amorphous (approximately 20 %) and related oxides of Mn, (about 26 % in the Odra tributaries 11 %). Copper is present mainly as associated with amorphous Fe oxides, both in the Odra River (34 %) and in its tributaries (53 %) and bounded with organic substances and/or amorphous sulfides or in residum (about 20 %). Chromium is present in SPM mainly in the form of amorphous Fe oxides (about 30 %). Detailed results were published in [19].

Conclusions

Metal pollution of the aquatic environment can be natural – caused by geology and geomorphology and/or is a result of human activities, therefore it is so important to analyze geology of the river bed and the catchment area as well as determine anthropogenic sources in the basin. Suspended matter seems to be the important indicator of the processes occurring in the basin and provide relevant information about anthropogenic metal pollution in riverin environment. The composition of river water is conditioned by a number of physical, chemical and biochemical processes. The most important mechanisms defining the migration of heavy metals between the solid and the solution are: sorption – desorption, precipitation – dissolution (treated as a special case of sorption), flocculation-agglomeration and the formation of complexes. Clay minerals, oxides and hydroxides of Fe and Mn, carbonates, organic matter and biological components are responsible for the accumulation of metals in the SPM. Result of SEM-EDS shows the presence of carbonates, mainly calcite, silicates – especially quartz and feldspars as well as illit and other clay minerals as well as antropogenical grains *eg* fly ash, Mn-Ca aluminosilicates in suspended matter of the Odra River. Obtained results allowed to recognize a variety of plankton species, most common are *Navicula lancelot, Stephanodiscus hantzschiin, Cyclotella meneghiniana and Nitzschia acicularis*. Widespread feldspar and quartz contain relatively low metal content, as opposed to clay minerals (fine fraction) and heavy minerals, which contain much higher concentration. Granulomeric SPM analysis shows that fine fraction (< 20 μm) dominates with average values of individual campaigns from 67 mass % in June 2000 to 84 mass % in November 1997 (after flood) [23]. TEM-EDX analyses identified following minerals in the SPM of the Odra River (fraction < 2 μm) – smectite/illite, beidellite, beidellite/montmorillonite, illite, kaolinite, chlorite, nontronite, montmorillonite and montmorillonite/vermiculite [23].

There were no significant changes depending on the season in the suspended matter concentration and metals amounts in the Odra river and its tributaries. High levels of metals in SPM, in particular, As and Cd were found in the upper course of the river from Chalupki to Raciborz and in the middle – from Glogow to Krosno Odrzanskie. Above-mentioned metals can be a significant threat to aquatic ecosystems due to harmfulness, toxicity and high mobility. The study showed extremely high Cd contamination of the river in all compartment – water, suspended matter and in sediment of the Odra River [19]. The significant source of metal in water and suspended matter seems to be the agricultural and industrial activity that takes place in the Odra Catchment Area. Analyzing metals in water and SPM (constant parameters of river water Eh, pH, salinity) it is evident from earlier studies of the Odra River that Cu, As, Cr, Ni and Zn was mainly transported by river water, while Cd, Pb and Fe by river suspended matter [19, 21]. It should be noted that highest concentrations of metals in the riverin water were found in the same locations where there are high contents of these metals in SPM. Comparison of metal content in SPM and sediment of the Odra river revealed similar values for the content of average concentrations in these components. My earlier research based on 5 Sampling Campaigns and over 50 sampling points during each sampling campaigns allow to conclude that changes in the concentrations of metals in sediments are “insignificant” in comparison with the suspended matter [24]. Suspended matter is more “flexible”. Therefore, it is proposed to consider SPM as the indicator of metal pollution of anthropogenic origin in the river system. Another reason it is less complicated procedure for collecting a representative sample compare to sediment as well as better homogeneity and less time-consuming analytical procedure. Information on total concentration of metals is not sufficient to assess their potential bioavailability and mobility, which depend on their chemical forms and transport phases. Selective chemical extractions are widely used to determine the different forms of metals in aquatic systems despite some uncertainties *eg* re-adsorption onto other phases during extraction. It seems very reasonable to measure the amount of mobile forms of selected metals – in particular metals that can be easily released into water *eg* Cd, As, Zn.

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CHARAKTERYSTYKA ZAWIESINY JAKO WSKAŹNIKA ZANIECZYSZCZENIA ANTROPOGENNEGO METALAMI SYSTEMU RZECZNEGO

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Abstrakt: Zawiesina jest ważnym wskaźnikiem procesów zachodzących w dorzeczu. Zanieczyszczenie środowiska wodnego metalami może być pochodzenia naturalnego, głównie jednak ma charakter antropogenny. Naturalnym źródłem metali w systemie rzecznym są określone formacje skalne i minerały ulegające wietrzeniu i erozji. Jakość i ilość zawiesiny jest uzależniona od ukształtowania i budowy geologicznej koryta rzecznego, wielkości dorzecza, jak również klimatu oraz okresów wegetacji. Rozpoznanie mineralogiczne i geochemiczne zawiesiny oraz określenie jej składu i genezy składników ją budujących jest niezbędne do oceny roli zawiesiny w akumulacji i transporcie metali śladowych w rzece. W tym celu przeprowadzone zostały badania SEM-EDS składu zawiesiny. Stwierdzono występowanie węglanów – głównie kalcytu oraz krzemianów i glinokrzemianów, a w szczególności kwarcu i skaleni potasowych. Uzyskane wyniki pozwoliły rozpoznać różnorodne gatunki planktonu, a w szczególności, takie jak *Navicula lancelota, Stephanodiscus hantzschiin, Nitzschia acicularis* oraz *Cyclotella meneghiniana.* W próbkach stwierdzono obecność znacznej ilości pyłów antropogennych. Dodatkowo przeprowadzono badania Ca, K i Mg. Stężenia pierwiastków wynosiły odpowiednio 71,5 mg/dm^3, 8,77 mg/dm^3, 18,37 mg/dm^3. Równolegle autorka prowadziła szczegółowe badania ilość zawiesiny i zawartość w niej metali. Badania wykazały znaczne zanieczyszczenia Cd, Zn i umiarkowane pozostałymi metalami ciężkimi (Pb, Ni, Cr, Fe, Cu, Mn) i As. W celu określenia mobilności przeprowadzono badania form związania metali w zawiesinie. Badania wykazały, że Cd, Zn i As stwarzają największe zagrożenie dla systemu rzeki Odry. Badania SEM-EDS oraz metali i ich form związania z wykorzystaniem ICP-MS pozwoliły na kompleksową ocenę zawiesiny jako potencjonalnego wskaźnika zanieczyszczenia antropogennego metalami systemu rzecznego.

Słowa kluczowe: zawiesina, metale ciężkie, Odra

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Katarzyna GRATA[1] and Małgorzata NABRDALIK[1]

EFFECT OF DIFFERENT CARBON SOURCES ON AMYLOLYTIC ACTIVITY OF *Bacillus* sp.

WPŁYW RÓŻNYCH ŹRÓDEŁ WĘGLA NA AKTYWNOŚĆ AMYLOLITYCZNĄ *Bacillus* sp.

Abstract: Studies on the amylolytic activity were carried out with used ten (10) *Bacillus* strains (*B. pumilus*, *B. cereus*, *B. mycoides* and *B. subtilis*), isolated from soil samples and water of Turawa Lake. The amylolytic activity was estimated on the basis of reduction in the intensity of the blue colour resulting from enzymatic hydrolysis of starch, in depending on the carbon sources and their concentration. The cultures were maintained at 30şC with the following substrates as carbon sources: potato starch, corn starch, maltose and glucose. Conducted research indicate, that among an analyzed strains the most active appear the *B. mycoides* G3 and *B. subtilis* G2. They preferred the maltose as the source of the carbon. Moreover, in comparison with all examined strains, *B. subtilis G2* showed the amylolytic activity on all tested media.

Keywords: *Bacillus* sp., amylolytic activity, potato starch, corn starch, maltose, glucose

Enzymes, including amylases have been reported to occur in microorganisms, although they are also found in plants and animals [1]. Most enzymes today (and probably nearly all in the future) are produced by microorganisms, such as bacteria, yeast and fungi. Among bacteria several species of *Bacillus* (*B. subtilis*, *B. licheniformis*, *B. cereus*, *B. amyloliquefaciens*) produce very active enzymes with ability to degradation of substrates such as cellulose, pectin, chitin and starch. All these bacteria are easily isolate from the natural environment. Amylase represent of the most important enzyme group and are great significance in present day for biotechnology [2–4].

Spectrum of applications of amylases has used in many sectors such as medical, and analytical chemistry [4–5]. They have also applied in the food processing, textile, paper and distilling industries, in agriculture and environmental protection [4, 6–7]. These enzymes account for about 30 % of the world's enzyme production [8].

The effect of the medium composition (the source of carbon and his concentration) on the level of amylase synthesis by selected *Bacillus* strains was examined.

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Materials and methods

The amylolytic bacteria were isolated from soil samples and water of Turawa Lake and screened for amylase production on Waksmana medium consisting of (g · dm^{-3}): agar – 20, soluble starch – 10, K_2HPO_4 – 1, NaCl – 1, $(NH_4)_2SO_4$ – 2, $CaCO_3$ – 5, pH 6.2. Amylolytic isolates were selected by flooding the agar plates with Gram's iodine solution. The selected strains (only the positive and the better zone formed strains) were taken for further experiments and kept on the nutrient agar at 4 ^{o}C. Bacterial phenotypic characterization by physiological and biochemical tests were performed according to the Bergey's Manual of Systematic Bacteriology [9] and API 50CHB system (bioMerieux, France).

Various carbon sources such as potato starch (P), corn starch (C) or maltose (M) in the range 1–5 % and glucose (G) (1 %) were evaluated for their influence on amylase production by supplemented as individual components to the production media. The medium (50 cm^3) was inoculated with a concentrated suspension of *Bacillus* strains (optical density of 2.0 at λ = 560 nm) and incubated at 30 ^{o}C on a rotary shaker at 110 rpm. After centrifugation at 4000 rpm for 20 min the supernatant of the culture was used to determine the amylolytic activity.

The amylolytic activity was estimated on the basis of reduction in the intensity of the blue colour resulting from enzymatic hydrolysis of starch according to the modified Fenela method [10]. The reaction mixture containing 0.2 % starch dissolved in potassium phosphate buffer (pH 7.0) and 2 cm^3 0.85 % NaCl was incubated at 30 ^{o}C for 5 min, following was added 1 cm^3 or 0.1 cm^3 of culture filtrate, then incubated at 37 ^{o}C for 30 min in a water bath. To this, 5 cm^3 of Lugols iodine was added and amylolytic activity was estimated after appropriate dilution and the absorbency was measured at λ = 560 nm against substrate blank with a spectrophotometer. On the basis of the obtained results, the amount of degrading of starch per 30 min at 37 ^{o}C was evaluated. One enzyme unit [U/cm^3] was defined as the amount of enzyme that catalysed the degrading of starch per min under the assay conditions.

Results and discussion

In this paper, *Bacillus* strains that are capable of growing on starch as the sole carbon source have been isolated. Based on its ability to production of amylase, *Bacillus* strains were chosen to study the performance of amylase during degradation of starch. The bacterium were identified as strains of *B. mycoides* (2 strains), *B. cereus* (3 strains), *B. pumilus* (4 strains) and *B. subtilis* (1 strain).

Potato starch, corn starch, maltose and glucose are major substrate considered for enzyme production in this study. The effect of different carbon sources on amylase production showed that each bacteria behaved differently. Figure 1 shows the enzymatic activity of the amylolytic *Bacillus* species that are capable of decomposition of potato starch.

From *Bacillus cereus* "group", the *B. mycoides G3* showed high enzyme release and 2.5 % concentration of potato starch was found to be optimum for the production of

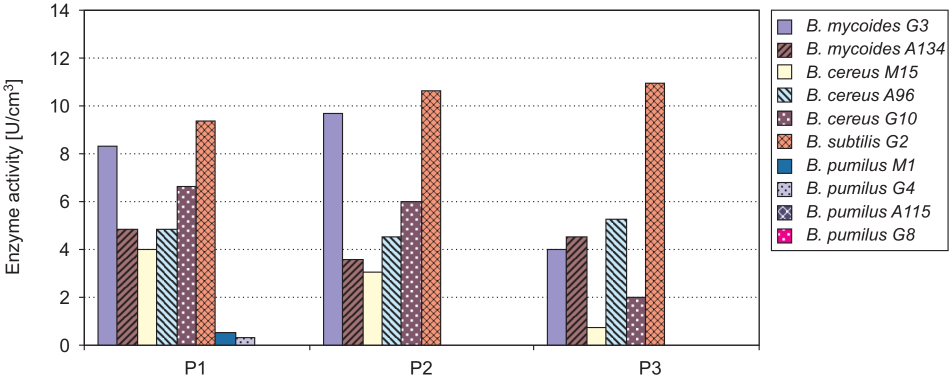

Fig. 1. Effect of different concentrations of potato starch (P1 – 1 %, P2 – 2.5 %, P3 – 5 %) on the amylolytic activity of *Bacillus* strains

amylase (9.66 U/cm^3). The amount of starch degrading was from 0.12 to 0.29 mg/cm^3 (Table 1). In the case of *Bacillus subtilis* "group" strain *B. subtilis G2* produced the highest yield of amylases (9.33–11.0 U/cm^3), spreading from 0.28 to 0.33 mg/cm^3 of the starch (Table1). In contrast to the other *Bacillus* strains, *B. pumilus G8* and *A115* strains did not produced amylase on this medium, whereas *B. pumilus* marked *M1* and *G4* appear the ability to degradation of starch only at 1 % concentration of potato starch (0.53 U/cm^3 and 0.33 U/ cm^3, respectively) (Fig. 1).

Table 1

Effect of different concentrations of potato starch and corn starch on amylolytic activity of *Bacillus* strains [mg/cm^3]

Bacillus strains	Medium with potato starch			Medium with corn starch		
	1 %	2.5 %	5 %	1 %	2.5 %	5 %
Bacillus mycoides G3	0.25	0.29	0.12	0.23	0.22	0.36
Bacillus mycoides A134	0.15	0.11	0.14	0.20	0.07	0.17
Bacillus cereus M15	0.12	0.09	0.02	0	0.03	0.04
Bacillus cereus A 96	0.15	0.14	0.16	0.14	0.12	0.11
Bacillus cereus G10	0.20	0.18	0.06	0.12	0.07	0.12
Bacillus subtilis G2	0.28	0.32	0.33	0.29	0.26	0.25
Bacillus pumilus M1	0.02	0	0	0.03	0.01	0.03
Bacillus pumilus G4	0.01	0	0	0	0	0
Bacillus pumilus A115	0	0	0	0	0	0
Bacillus pumilus G8	0	0	0	0	0	0

The studies with different concentrations of corn starch were similar to the results obtained on the medium enrichment in potato starch. The effect of corn starch on amylase synthesis by *Bacillus* sp. was also investigated (Fig. 2).

Among the all *Bacillus* sp. tested, only two strains *B. mycoides G3* and *B. subtilis G2* revealed the enzymatic abilities in the highest degree. The enzymatic activity ranged

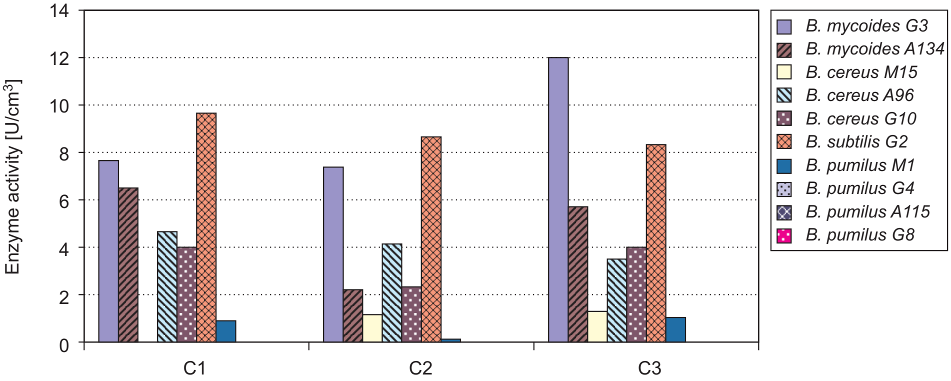

Fig. 2. Effect of different concentrations of corn starch (C1 – 1 %, C2 – 2.5 %, C3 – 5 %) on the amylolytic activity of *Bacillus* strains

from 7.33 U/cm^3 to 12.0 U/cm^3 and from 8.33 U/cm^3 to 9.66 U/cm^3, respectively. The maximum degree of starch decomposition were observed in the presence of 5 % (0.36 mg/cm^3) and 1 % (0.29 mg/cm^3) concentration of corn starch, respectively. It has also been found that *B. pumilus* strains marked *A115, G4* and *G8* did not secrete of the enzymes on this medium (Fig. 2, Table 1).

The influence of the maltose on the decomposition of starch by *Bacillus* sp. are presented in the Fig. 3 and Table 2. Based on the obtained results, the highest ability to the amylase synthesis were found for *B. subtilis G2* and *B. mycoides G3*. The decomposition of starch by this strains were from 0.18 mg/cm^3 to 0.40 mg/cm^3 and from 0.30 mg/cm^3 to 0.40 mg/cm^3, respectively. Moreover, the maximum level of amylase synthesis was observed on the medium supplemented with 1 % (13.33 U/cm^3) and 5 % (13.33 U/cm^3) maltose, and it proved to be a good substrate for this enzyme synthesis. It was found that the decrease in the release of the enzyme by *B. mycoides* G3 and increase in the case of *B. subtilis G2*, occurred when the concentration of maltose

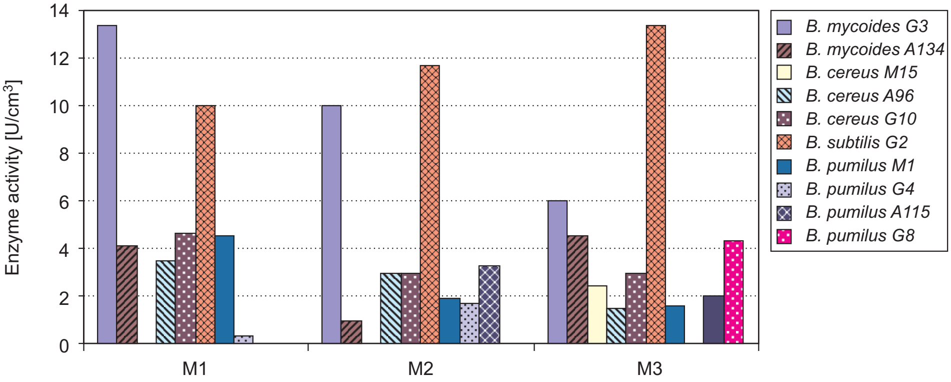

Fig. 3. Effect of different concentrations of maltose (M1 – 1 %, M2 – 2.5 %, M3 – 5 %) on the amylolytic activity of *Bacillus* strains

was increased. However, strains of *B. cereus M15* and *B. pumilus G8* revealed the enzymatic activity when maltose was added at 5 % concentration (2.46 U/cm^3 and 4.33 U/cm^3, respectively). Other *Bacillus* strains showed 2–3 fold lower amylolytic activity than two the most active strains.

Table 2

Effect of different concentrations of maltose and glucose
on amylolytic activity of *Bacillus* strains [mg/cm^3]

Bacillus strains	Medium with maltose			Medium with glucose
	1 %	2.5 %	5 %	1 %
Bacillus mycoides G3	0.40	0.30	0.18	0.23
Bacillus mycoides A 134	0.13	0.05	0.14	0.11
Bacillus cereus M15	0	0	0.08	0.07
Bacillus cereus A 96	0.11	0.09	0.04	0.15
Bacillus cereus G10	0.14	0.09	0.09	0.15
Bacillus subtilis G2	0.03	0.35	0.40	0.46
Bacillus pumilus M1	0.14	0.06	0.05	0.11
Bacillus pumilus G4	0.01	0.05	0	0.27
Bacillus pumilus A115	0	0.10	0.06	0.16
Bacillus pumilus G8	0	0	0.13	0.08

Figure 4 presented the yield of amylase produced by *Bacillus* sp. on medium with glucose.

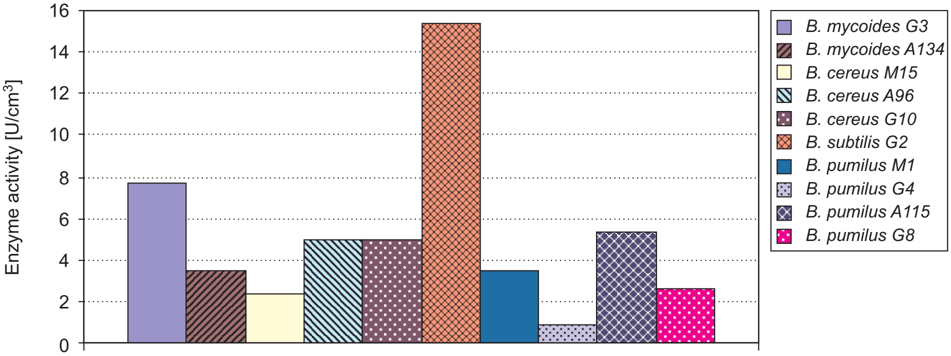

Fig. 4. Effect of 1 % concentrations of glucose on the amylolytic activity of *Bacillus* strains

Among the all strains of *Bacillus*, *B. subtilis G2* demonstrated the highest activity on the medium with glucose (15.33 U/cm^3). *Bacillus mycoides G3* that belong to the "cereus group" showed 2-fold lower activity (7.66 U/cm^3) than stated in case of *B. subtilis G2*. The amount of starch decomposed was 0.49 mg/cm^3 and 0.23 mg/cm^3, respectively. Moreover, we observed an over 3-fold decrease in the amylolytic activity of the *B. cereus* strains marked *A96* and *G10* and *B. pumilus A 115*, but almost 4–5 fold decrease in the activity of the *B. cereus* strains marked *M15* and *G8* towards glucose as a substrate, compared with the most active strains (Fig. 4, Table 2).

The addition of carbon source in the form of either monosaccharides or polysaccharides could influence on the production of enzymes [4, 6, 11]. Use of media differenting in composition of nutritive component for cultivation of bacteria has allowed establishing that in the media rich in available monomers (glucose, amino acids) the bacteria absorb these monomers, whereas in poorer media they produce hydrolytic enzymes for degrading of highly molecular substrates [12]. Santhos et al [13] showed that with some carbon sources an inverse relationship exists between the growth and the amount of amylase produced. Maltose, starch and citrate did not conform to this relationship in that these substrates stimulated amylase formation. Similarly, it has been reported by Saxena et al [14] and Ajayi et al [6], that amount carbon sources, soluble starch, maltose, corn starch and xylose were found to support amylase production. These results are in agreement with the report of many authors [*eg* 2, 4] who reported maximum amylase production *eg* by *B. cereus*, *Bacillus K-12,* when starch was used as carbon source.

The reports of many authors show that the efficiency of the amylase synthesis of some microorganisms is significantly inhibited by the presence of monosaccharydes or disaccharydes. The enzyme formation with the other carbon sources (glucose, lactose, mannose, galactose) were much lower compared with that with starch and maltose [13]. Sudharhsan et al [15] observed that glucose and fructose represses the production of amylase. Similarly, it has been reported by Santhos et al [13] and Lin et al [16] that synthesis of carbohydrate degrading enzyme in most species of genus *Bacillus* sp. leads to catabolic repression by readily metabolizable substrates such as glucose and fructose. Teodoro et al [17] found, that the addition of glucose (0.5 %) to the culture diminished greatly the synthesis of amylase. These results are similar to the findings of Aiyer [18], who observed that nonmetabolizable sugars like arabinose, raffinose, sucrose and galactose did not support amylase production.

Ability to the degradation of the starch depends not only on the kind of the source of carbon and its concentration, but also from species or the *Bacillus* strain. The effect of different carbon sources on amylase production applied in own investigations showed that each bacteria behaved differently. Similar results have also been obtained by other researchers. Jamuna et al [19] reported that α-amylase production by *B. subtilis* was higher with glucose than with starch. According Sarikaya et al [20], *B. amyloliquefaciens I* intensively produces amylolytic enzymes with starch, moreover *B. amyloliquefaciens II* with sucrose as the sole carbon source. In contrast, carbon sources such as glucose, maltose and starch did not enhance α-amylase production by thermophilic *B. coagulans* [21]. Moreover, Aiyer [18] using 1 % of different soluble sugars, amylase production by *B. licheniformis* was highest in fructose and maltose medium and in using 1 % of potato starch. Therefore, our results are in good agreement with the findings in these studies.

Conclusion

The obtained results indicate that ability to the decomposition of the starch depends not only on the kind of the source of carbon and its concentration, but also from species or the *Bacillus* strain. The effects of potato starch, corn starch and maltose in the range 1–5 % and glucose (1 %) on the enzyme production showed that each bacteria behaved differently. In the medium containing potato starch, corn starch, maltose or glucose the maximum production of amylase were archived for *B. subtilis G2* and *B. mycoides G3* from all *Bacillus* strains tested. Among the carbon sources added to basal medium, maltose was found as the best substrate for enzyme production by *B. mycoides G3*, however glucose and maltose for *B. subtilis G2.* Whereas, the lowest activity were observed for *B. pumilus A115* and *G8* strains. They demonstrated the lowest activity only on the medium with maltose, but did not show any activity on the medium containing of potato starch or corn starch.

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WPŁYW RÓŻNYCH ŹRÓDEŁ WĘGLA NA AKTYWNOŚĆ AMYLOLITYCZNĄ *Bacillus* sp.

Samodzielna Katedra Biotechnologii i Biologii Molekularnej
Uniwersytet Opolski

Abstrakt: Celem badań była ocena aktywności amylolitycznej 10 szczepów *Bacillus* sp. (*B. pumilus*, *B. cereus*, *B. mycoides* i *B. subtilis*) wyizolowanych z gleby i wody z jeziora Turawa. Na podstawie stopnia zmniejszenia się zabarwienia z jodem oznaczono ilość rozłożonej skrobi, w zależności od źródła węgla i jego koncentracji. Hodowle prowadzono w temperaturze 30 ^{o}C z zastosowaniem następujących źródeł węgla: skrobia ziemniaczana, skrobia kukurydziana, maltoza oraz glukoza. Uzyskane wyniki badań wykazały, iż spośród badanych szczepów *Bacillus sp*. najbardziej aktywnymi okazały się *B. mycoides G3* i *B. subtilis G2*, które preferowały maltozę jako źródło węgla. Ponadto, w porównaniu do wszystkich szczepów, *Bacillus subtilis G2* wykazał największą aktywność na wszystkich testowanych podłożach.

Słowa kluczowe: *Bacillus* sp., aktywność amylolityczna, skrobia ziemniaczana, skrobia kukurydziana, maltoza, glukoza

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SOIL CONTAMINATION WITH ZINC, CADMIUM AND LEAD IN THE CITY OF ZABRZE

ZANIECZYSZCZENIE GLEBY CYNKIEM, KADMEM I OŁOWIEM NA TERENIE ZABRZA

Abstract: Heavy metal concentrations were evaluated in topsoil (0–10 cm) in the city of Zabrze. Soil samples were taken from 71 sites distributed evenly throughout the city, in the vicinity of emitters, roads, residential areas and parks, representing various biotopes – mainly green belts, squares, fields, brownfields, lawns, forests and meadows. Average Zn concentrations ranged from 31.7 mg · kg^{-1} (meadows) to 2057.1 mg · kg^{-1} (brownfields). The highest Cd concentrations were also found in brownfields. The average Cd concentrations ranged from 0.15 up to 13.1 mg · kg^{-1}. The Pb concentrations ranged from 31.5 to 520 mg · kg^{-1} and were the lowest in meadows. The highest heavy metal pollutions were in soil samples collected in the vicinity of roads and industrial plants. Results indicate the necessity of soil pollution mapping in cities, especially for proper human risk assessment and for the prevention of further pollution spread.

Keywords: heavy metals, zinc, lead, cadmium, pollution

Introduction

Urban soils are known to have peculiar characteristics, such as unpredictable layering, poor structure and high concentrations of trace elements [1]. Soils in urban environments have a highly variable and often unknown history as a result of differences in land use, transfer between sites and mixing in connection with excavations, addition of new soil material etc. [2].

In urban soils the anthropogenic sources of heavy metals include traffic emissions (vehicle exhaust particles, tyre wear particles, weathered street surface particles, brake lining wear particles), industrial emissions (power plants, coal combustion, metallurgical industry, auto repair shops, chemical plants, etc.), domestic emissions, weathering of buildings and pavement surfaces, atmospheric deposition and so on [3].

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Heavy metals are considered to be one of the main sources of environmental pollution and have a significant effect on soil ecological quality [1]. An assessment of the environmental risk due to soil pollution is of particular importance because heavy metals, which are potentially harmful to human health, persist in soils for a very long time [4]. Cadmium, lead, and zinc are good indicators of contamination in soil because they appear in gasoline, vehicle exhaust, car components, industrial emissions etc. [5].

The aim of this study was to investigate the concentrations of selected heavy metals (Zn, Cd, Pb) in topsoil samples in the city of Zabrze (southern Poland, Silesia province) as a basis for assessment of the degree of anthropopressure.

Material and method

The investigation was carried out on topsoil in the city of Zabrze in 2010. Samples of soil (from the level 0–10 cm) were taken from 71 sites (Table 1) located evenly throughout the city in the vicinity of emitters, roads, residential areas and parks. The investigated areas represented various biotopes (green belts, squares, fields, brownfields, lawns, forests and meadows).

Table 1

Sampling sites

Sampling sites no.	Latitude	Longitude	Sampling sites no.	Latitude	Longitude
1	50°17′54.17″N	18°47′18.14″E	36	50°22′46.51″N	18°48′39.20″E
2	50°18′7.83″N	18°47′18.45″E	37	50°21′43.26″N	18°49′0.06″E
3	50°18′18.86″N	18°46′57.42″E	38	50°22′5.36″N	18°47′25.30″E
4	50°15′36.98″N	18°45′36.36″E	39	50°17′27.57″N	18°47′33.83″E
5	50°15′20.97″N	18°46′9.51″E	40	50°16′59.18″N	18°47′21.50″E
6	50°17′55.97″N	18°47′58.09″E	41	50°16′37.13″N	18°47′1.36″E
7	50°17′39.65″N	18°48′30.99″E	42	50°16′18.92″N	18°46′37.75″E
8	50°17′41.04″N	18°49′27.14″E	43	50°15′56.83″N	18°45′58.89″E
9	50°18′6.31″N	18°50′15.07″E	44	50°16′26.80″N	18°47′42.71″E
10	50°18′12.63″N	18°49′36.53″E	45	50°16′8.10″N	18°47′45.96″E
11	50°18′15.95″N	18°48′53.73″E	46	50°16′48.51″N	18°47′51.75″E
12	50°18′2.84″N	18°48′14.33″E	47	50°17′53.67″N	18°46′47.49″E
13	50°18′25.81″N	18°46′27.11″E	48	50°17′28.41″N	18°46′57.95″E
14	50°18′19.17″N	18°46′0.86″E	49	50°16′49.49″N	18°48′29.50″E
15	50°18′17.62″N	18°45′26.63″E	50	50°16′51.30″N	18°49′24.12″E
16	50°18′20.73″N	18°44′25.18″E	51	50°17′18.39″N	18°48′55.67″E
17	50°18′41.32″N	18°44′45.44″E	52	50°19′5.03″N	18°46′35.59″E
18	50°18′40.21″N	18°45′19.93″E	53	50°19′37.93″N	18°46′25.38″E
19	50°18′43.01″N	18°46′2.93″E	54	50°20′2.83″N	18°46′1.52″E
20	50°18′40.40″N	18°47′8.24″E	55	50°19′41.77″N	18°51′43.02″E
21	50°19′1.03″N	18°47′5.76″E	56	50°20′15.90″N	18°49′36.41″E

Table 1 contd.

Sampling sites no.	Latitude	Longitude	Sampling sites no.	Latitude	Longitude
22	50°19′29.31″N	18°47′10.53″E	57	50°20′35.53″N	18°49′12.37″E
23	50°19′56.08″N	18°46′51.09″E	58	50°19′40.10″N	18°49′18.64″E
24	50°20′21.10″N	18°46′46.38″E	59	50°16′58.24″N	18°46′44.39″E
25	50°20′46.48″N	18°46′11.33″E	60	50°16′51.58″N	18°46′1.09″E
26	50°21′8.73″N	18°46′7.72″E	61	50°17′4.51″N	18°45′19.46″E
27	50°21′37.18″N	18°46′11.06″E	62	50°17′40.55″N	18°45′52.87″E
28	50°22′20.77″N	18°46′49.93″E	63	50°17′58.27″N	18°46′8.32″E
29	50°18′40.62″N	18°47′53.36″E	64	50°17′58.35″N	18°44′45.30″E
30	50°19′6.49″N	18°48′55.57″E	65	50°19′13.39″N	18°44′35.09″E
31	50°19′29.44″N	18°49′50.37″E	66	50°19′19.56″N	18°45′27.68″E
32	50°19′51.08″N	18°50′34.86″E	67	50°19′42.02″N	18°45′37.10″E
33	50°21′29.03″N	18°47′43.74″E	68	50°20′11.64″N	18°45′4.94″E
34	50°21′49.80″N	18°48′4.17″E	69	50°19′36.38″N	18°44′54.99″E
35	50°22′21.57″N	18°48′13.26″E	70	50°20′18.77″N	18°46′15.90″E
			71	50°20′53.80″N	18°48′7.33″E

The topsoil samples were air-dried and sieved through a 1 mm sieve. Metals were extracted with 10 % HNO_3 [6]. The concentrations of metals (Zn, Cd and Pb) were measured by flame absorption spectrometry (Unicam 939 Solar). The quality of the analytical procedures was controlled using reference material (Certified Reference Material CTA-OTL-1 Oriental Tobacco Leaves). Fig. 1–3 were drawn using the Surfer 8 program.

Results and discussion

Zn, Pb and Cd contaminations in Zabrze based on metal content in soil was presented by means of isolines in the Fig. 1–3. The lowest values of concentration were marked with the bright color and the highest with the dark color. Contents of Zn, Pb and Cd in upper layer of the soil in various biotopes were presented by Fig. 4–6.

The average Zn soil concentrations in different countries fall within the range of 30–120 mg · kg^{-1}. The average Zn content for non-polluted soils in Poland is 40 mg · kg^{-1} and the permitted Zn concentration in soil is 300 mg · kg^{-1} [7].

In our study, Zn concentrations ranged from 31.69 to 2057.16 mg · kg^{-1}. The mean Zn soil content was 242.27 mg · kg^{-1}. The lowest Zn content was observed in the soils from meadows and forests, and the highest Zn content was recorded near the defunct landfill of the Zabrze smelter, with the limit value exceeded many times. The allowable concentration of zinc in Polish soils was also exceeded in 16 of the 70 research sites. For comparison, Indeka and Karaczun [8] in the city of Katowice reported significant exceeding of the soil limit values (680.0 mg · kg^{-1}). In the Krakow conurbation, the average Zn soil concentration was 104.2 mg · kg^{-1}, ranging from 36.1 to 732.0 mg · kg^{-1}

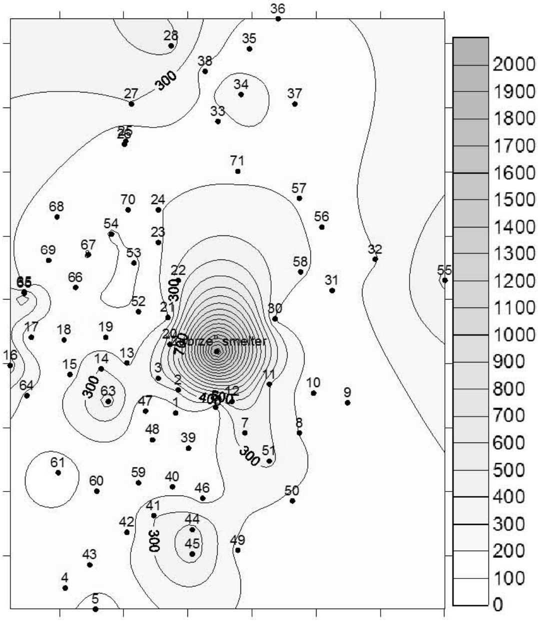

Fig. 1. Zn contamination in Zabrze based on metal content in soil [mg · kg^{-1} d.m.]

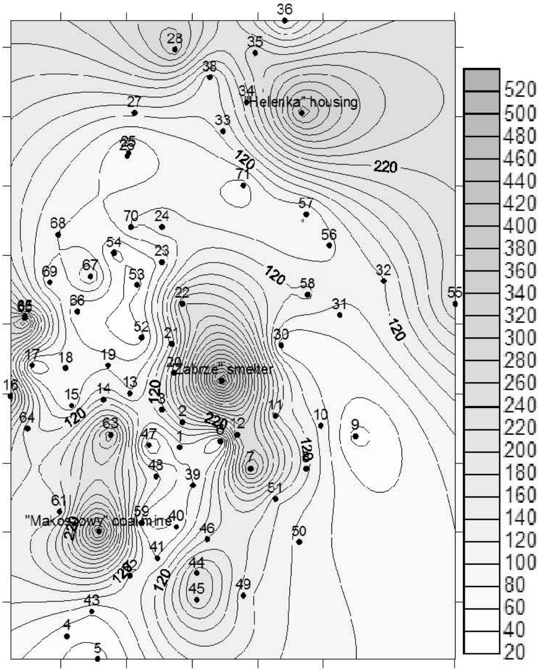

Fig. 2. Pb contamination in Zabrze based on metal content in soil [mg · kg^{-1} d.m.]

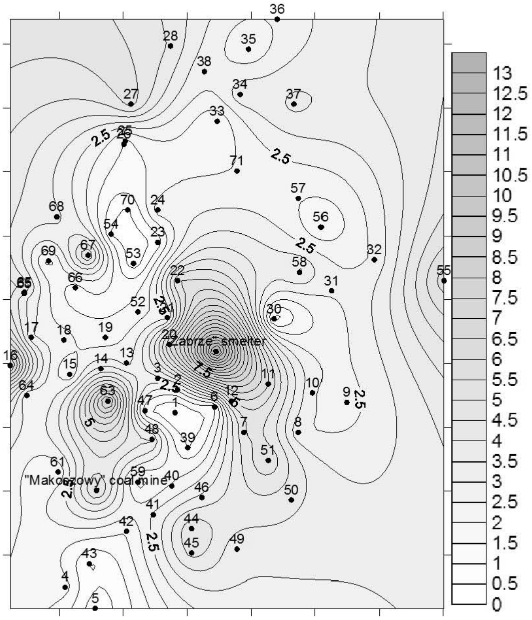

Fig. 3. Cd contamination in Zabrze based on metal content in soil [mg · kg^{-1} d.m.]

[9]. Average Zn content obtained in our study was much higher than that found by Grzebisz et al [4] in Poznan (72.98 mg · kg^{-1}) and Greinert [10] in the soils in the city of Zielona Gora (18.30 mg · kg^{-1}). Also Marjanovic et al [5] in Belgrade, Linde et al [2] in Stockholm and Lee et al [11] in Hong Kong observed lower Zn soil concentrations than in our current paper.

Pb content in soil closely depends on mineralogical and granulometric composition and derivation of soil bedrocks while at the same time occurrence of this element in topsoil is primarily connected with anthropogenic factors. Pb content in unpolluted soils should amount to 20 mg · kg^{-1}, although Gambus and Gorlach [9] increase this range to 25 mg · kg^{-1}, giving also Pb content for the polluted soils within 4560 mg · kg^{-1}.

Permissible Pb concentration in soil is 100 mg · kg^{-1} [7], while the average Pb content in topsoils in Zabrze was 134.27 mg · kg^{-1}. In the majority of biotopes admissible Pb concentrations were exceeded. Also Lukasik et al [12] in studies on the area of Piekary Slaskie found a 4–25 times greater Pb concentration than permissible standards. Kabata-Pendias, Pendias [7] state that in Upper Silesia Pb concentration can reach from 6000 to 8000 mg · kg^{-1} of soil. A much lower Pb content was observed in soils in Krakow conurbation by Pasieczna [13] – 45.52 mg · kg^{-1}.

To the most Cd polluted soils can be found in southern Poland, especially Silesia and Malopolska Districts. From monitoring studies of Terelak et al [14] it results that soils of higher Cd content than natural make up 67.3 % of soils in Silesia and 45.3 % in Malopolska. The range of mean Cd content in world soils is within the 0.2–1.05 mg · kg^{-1} range, and in Poland it is 0.2 mg · kg^{-1} [7]. The maximum limit for Cd in soils

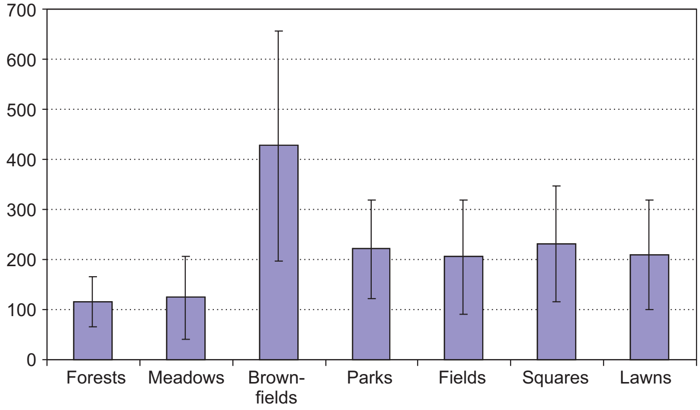

Fig. 4. Content of Zn in the upper layer of soil in various biotopes [mg · kg^{-1} d.m.]

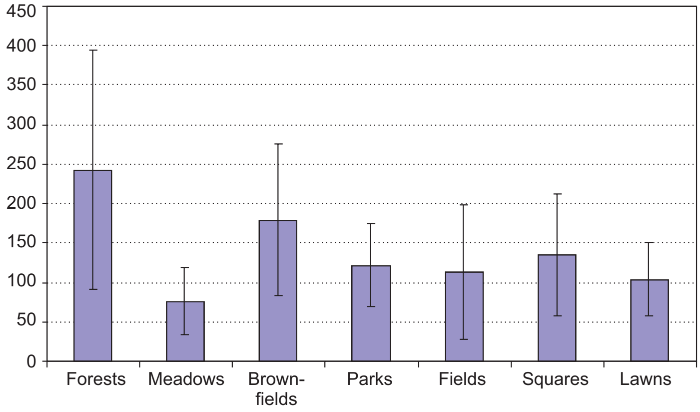

Fig. 5. Content of Pb in the upper layer of soil in various biotopes [mg · kg^{-1} d.m.]

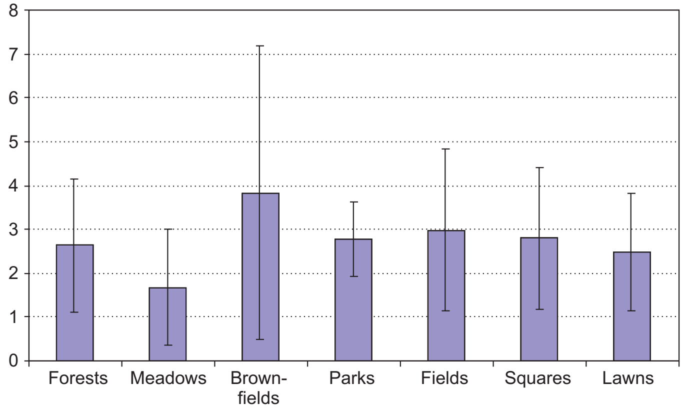

Fig. 6. Content of Cd in the upper layer of soil in various biotopes [mg · kg^{-1} d.m.]

is 4 mg · kg^{-1} (Polish Journal of Laws). At low pH values (4.5–5.5) Cd becomes very soluble and mobile. In surface environments, more than 90 % of Cd comes from anthropogenic sources [13, 15]. In our study, the average Cd content in soils was 2.87 mg · kg^{-1}, with the highest accumulation, exceeding the permissible content, near the defunct Zabrze Smelter (13.14 mg · kg^{-1}) and north of the "Makoszowy" coal mine. At the other sites and biotopes Cd did not exceed the permissible limit. Definitely lower cadmium content than the obtained in our study, was recorded by Arasimowicz [16] in Krakow conurbation (0.85 mg · kg^{-1}), Grzebisz et al [4] in soils in Poznan (0.755 mg · kg^{-1}), Linde et al [2] in Stockholm (0.40 mg · kg^{-1}) and De Miguel et al [17] in Madrid (0.14 mg · kg^{-1}).

The content of Zn, Pb and Cd in the soil within the city of Zabrze is highly variable. The highest heavy metals pollution was found in the soils samples collected in the vicinity of roads and industrial plants in the city. In general, pollution level mapping is necessary especially for proper human risk assessment and for further pollution spread prevention.

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ZANIECZYSZCZENIE GLEBY CYNKIEM, KADMEM I OŁOWIEM NA TERENIE ZABRZA

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Abstrakt: Oceniano zanieczyszczenie wierzchniej warstwy gleby na terenie Zabrza. Próbki gleby pobierano z 71 stanowisk równomiernie rozłożonych na terenie tego miasta: w pobliżu emitorów zanieczyszczeń, tras komunikacyjnych, z terenu osiedli mieszkaniowych, parków. Stanowiska badań reprezentowane były przez różne biotopy m.in. pasy zieleni, skwery, pola uprawne, nieużytki, trawniki, lasy i łąki. Średni poziom Zn mieścił się w granicach od 31,7 (łąka) do 2057,1 (nieużytki) mg · kg^{-1}. Najwyższe stężenia Cd stwierdzono w próbkach gleby pobieranych na terenie nieużytków. Średnia zawartość Cd wahała się od 0,15 do 13,1 mg · kg^{-1}. Najniższe koncentracje Pb stwierdzono w próbkach gleby pobieranych na łąkach. Średni poziom zanieczyszczenia tym pierwiastkiem mieścił się w granicach od 31,5 do 520 mg · kg^{-1}. Najwyższe poziomy analizowanych metali ciężkich wykazano w próbkach gleby pobieranych w pobliżu emitorów zanieczyszczeń i tras komunikacyjnych. Tworzenie mapy zanieczyszczeń wydaje się być konieczne i pomocne w oszacowaniu ryzyka narażenia zdrowia ludzi, a także może posłużyć w zapobieganiu dalszego rozprzestrzeniania się zanieczyszczeń.

Słowa kluczowe: metale ciężkie, cynk, ołów, kadm, zanieczyszczenie

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ACCUMULATION OF SELECTED METALS IN THE BOTTOM SEDIMENTS OF THE POND IN SZCZYTNICKI PARK IN WROCLAW

KUMULACJA WYBRANYCH METALI W OSADACH DENNYCH STAWU W PARKU SZCZYTNICKIM WE WROCŁAWIU

Abstract: The study was designed to establish the pollution of the water and bottom sediments as well as the accumulation rates of selected metals (lead, cadmium, zinc, copper, nickel) in the bottom sediments of the pond in Szczytnicki Park in Wroclaw, Poland. Samples for the study were taken from eight locations on four occasions during a 12-month period: in spring (24 April 2008), summer (19 July 2008), autumn (18 November 2008), winter (10 February 2009). The following were determined for the water: temperature, reaction, total hardness and selected metals (Zn, Cu, Cd, Pb, Ni). For the bottom sediments the content and accumulation of the above metals were established. The accumulation rates of the studied metals in the bottom sediments were found to be arranged as follows: Ni > Cu > Zn > Pb > Cd, whereas metal concentrations in the bottom sediments were: Zn > Cu > Ni > Pb > Cd. Lead and cadmium had the lowest accumulation rates and contents in the bottom sediments. The water and bottom sediments covered by the study were found not to be polluted with metals.

Keywords: lead, cadmium, zinc, copper, nickel, bottom sediments, accumulation, the Szczytnicki pond

The pond in the Szczytnicki Park in Wroclaw forms part of the Odra old river-bed. It may be supplied with water from the Odra indirectly, via the Japanese Garden pond. Most pollutants carried by water are deposited in bottom sediments. Knowledge of the phenomena and processes occurring between water and bottom sediments, which are in constant contact with each other, is of extreme importance. Sediments act as a regulator of the physicochemical properties of water. The chemical composition of sediments is affected by many factors, the most important of which is the geological structure of soil [1, 2]. The composition is also influenced by chemical compounds present in the water that accumulate in the sediments. Water often acts as a receptor of particles of organic matter from plants growing nearby. The pond covered by the study is located in a park

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and surrounded by deciduous trees, which periodically feed organic matter into the reservoir, which sometimes leads to blooming [3].

Both the water and the sediments retain and accumulate biogens, suspensions and highly toxic substances, such as metals, which seriously deteriorate the water environment [4–6]. Whether accumulation poses a threat may be assessed by calculating the accumulation rate and the amounts of metals accumulated.

The study in question was to determine metal accumulation in the bottom sediments of the pond in the Szczytnicki Park in Wroclaw.

Material and methods

The study material consisted of the water and bottom sediments from the pond, which has an area of 0.18 ha and the average depth of 1 m, and is located from 51°06′ north and 17°04′ east to 51°06′ north and 17°04′ east. Analytic material was collected in four seasons between 2008 and 2009 on eight different sites:

- Site 1 – 51°06′49.61″ N 17°04′58.70″ E
- Site 2 – 51°06′47.33″ N 17°04′58.48″ E
- Site 3 – 51°06′47.83″ N 17°04′56.55″ E
- Site 4 – 51°06′45.09″ N 17°04′51.88″ E
- Site 5 – 51°06′42.82″ N 17°04′48.52″ E
- Site 6 – 51°06′43.77″ N 17°04′47.45″ E
- Site 7 – 51°06′43.77″ N 17°04′47.45″ E
- Site 8 – 51°06′38.79″ N 17°04′46.58″ E.

The following parameters were measured directly on the sites:

- temperature using a Slandi TC 204 electronic thermometer;
- electrolytic conductivity using electrometer [7];
- reaction using electrometric method [8];
- dissolved actual oxygen using Hanna Instruments 9143 oxygen probe [9].

The other parameters were measured under laboratory conditions:

- total hardness [10];
- Zn, Cu, Cd, Pb, Ni [11].

Bottom sediment samples were collected at the same sites by means of an Ekman grab. Hydrated sediments were dried in room temperature, sieved through a 1-mm mesh sieve and pounded in a porcelain mortar. The sediments were then subjected to wet mineralization with a mixture of acids in a MARS-5 oven. Metal contents (Ni, Cd, Pb, Zn, Cu) in the mineralizate were determined using an atomic absorption spectrophotometry unit AAS-1N (Zeiss Jena) [12]. Obtained results were statistically analysed using Statistica 8.0 programme.

Results and discussion

Water temperature in the pond was ranging between 1.7 °C and 20.5 °C which is a standard temperature for Polish waters. The surface water temperature depends on the season (in summer 20 °C and more while in winter 0 °C) [13].

Water reaction of the Szczytnicki pond was ranged between 7.4 and 7.6. The average water hardness of the Szczytnicki pond was between 178.5–196.3 mg · $CaCO_3$ · dm^{-3}.

The average zinc content in water of the Szczytnicki Park pond was 0.0176 mg · dm^{-3} (Table 1), which is ten times less than that determined for south-west Poland in the 1980s by Szulkowska-Wojaczek et al [14].

Table 1

The metals concentration in water of the Szczytnicki pond

Metal	Season	Average	Min	Max	Standard deviation
Zn	spring	0.0175	0.0058	0.0367	0.0114
	summer	0.0085	0.0012	0.0235	0.0070
	autumn	0.0158	0.0012	0.0387	0.0114
	winter	0.0288	0.0161	0.0487	0.0120
Cu	spring	0.0076	0.0062	0.0117	0.0017
	summer	0.0026	0.0014	0.0037	0.0008
	autumn	0.0036	0.0018	0.0070	0.0017
	winter	0.0074	0.0038	0.0112	0.0027
Cd	spring	0.0004	0.0000	0.0011	0.0004
	summer	0.0002	0.0000	0.0004	0.0001
	autumn	0.0007	0.0000	0.0010	0.0004
	winter	0.0019	0.0013	0.0032	0.0007
Pb	spring	0.0026	0.0000	0.0126	0.0047
	summer	0.0004	0.0000	0.0015	0.0006
	autumn	0.0038	0.0012	0.0075	0.0020
	winter	0.0092	0.0060	0.0136	0.0029
Ni	spring	0.0007	0.0000	0.0012	0.0004
	summer	0.0011	0.0001	0.0023	0.0007
	autumn	0.0042	0.0032	0.0048	0.0005
	winter	0.0045	0.0025	0.0065	0.0015

In 2000 Karczewska et al [15] conducted a study regarding the presence of heavy metals in the soils in the Szczytnicki Park in Wroclaw. Individual metal concentrations in 2000 were as follows: 60–435 mgPb · kg^{-1}, 170–720 mgZn · kg^{-1}, 0.05–4.5 mgCd · kg^{-1}, and 40–570 mgCu · kg^{-1}. The values found for individual metals did not meet the criteria set by the State Environmental Inspection (PIOS) as permissible for public or recreational areas [15–17].

Zinc is necessary for organisms to grow, but its excess is harmful, also to fish. According to Liebmann [18] zinc is toxic to fish at concentrations of 0.1–2.0 mg · dm^{-3}, while at a concentration of 0.1 mg · dm^{-3} it hinders self-purification [18]. At the concentration discovered in the pond, zinc is not a threat to fish. The average zinc concentration in the water was the highest out of all the metals examined.

Tests done by PIOS in 2007 showed that the arithmetic mean zinc concentration in 125 lakes amounted to 92 mgZn · kg^{-1}. During the study in question the measured concentration at eight sites was four times smaller, at nearly 25 mgZn · kg^{-1} (Table 2).

Table 2

The metal concentration in bottom sediments of the Szczytnicki pond

Metal	Season	Average	Min	Max	Standard deviation	Bottom sediments concentration
Zn	spring	17.88	6.56	29.69	8.44	BBC
	summer	25.44	5.89	49.04	14.98	BBC
	autumn	28.61	8.13	54.33	16.74	BBC
	winter	25.88	7.53	70.90	21.08	BBC
Cu	spring	6.40	3.48	10.86	2.80	0
	summer	7.89	3.47	12.74	3.41	0
	autumn	13.20	2.74	49.67	16.32	+
	winter	4.76	1.88	8.04	2.61	0
Cd	spring	0.56	0.50	0.63	0.04	0
	summer	0.60	0.45	0.72	0.08	0
	autumn	0.16	0.00	0.27	0.11	BBC
	winter	0.21	0.15	0.32	0.07	BBC
Pb	spring	3.66	1.35	6.30	1.76	BBC
	summer	5.64	2.49	10.26	2.72	BBC
	autumn	6.06	1.39	11.22	3.63	BBC
	winter	5.88	0.00	25.52	8.31	0
Ni	spring	8.26	3.20	12.90	3.75	0
	summer	12.23	5.65	17.33	3.79	+
	autumn	5.03	1.18	9.79	2.93	0
	winter	3.87	1.43	6.99	2.30	0

BBC – below background concentration; (0) – unpolluted sediments; (+) – little polluted sediments; (++) – polluted sediments; (+++) – heavy polluted sediments.

The presence of metals in soils in the Szczytnicki Park in Wroclaw is also of importance to surface and underground water, to bottom sediments and plants. In 2000 Karczewska et al [15] showed that zinc concentration in the soil ranged between 170 and 720 mgZn · kg^{-1}. In a 2005 study by Licznar the metal content in the humus oscillated between 46 and 750 mgZn · kg^{-1} [16, 17]. The concentration of the element in the bottom sediment samples collected for the study was lower than that in the soil. This may be caused by its poor permeation from the soil into the park plants and so by bigger amounts of it than of other metals being carried into the water, and by poor leaching by the water over the sediments. According to the bottom sediments classification based on geochemical criteria, in terms of zinc content the sediments in question belong to purity class I, because at none of the sampling sites did the concentration exceed 200 mgZn · kg^{-1} [19] and was almost like in bottom sediment from Dubai creek [20] lower then in bottom sediments of Black Sea [21] or in the Selenga River sediments [22], mostly lower then in bottom sediments from estuary in Argentina [23].

The average annual rate of Zn accumulation in bottom sediments was calculated at $1.4 \cdot 10^{-3}$.

The research done in the 1980s by Szulkowska-Wojaczek et al [14] showed that waters in south-west Poland had an average Cu concentration of 0.011 mgCu · dm^{-3}, which is approximately the same as that found in the Szczytnicki pond in question in 2008/2009.

Only sometimes the Cu content values recorded throughout the year only slightly exceeded 0.01 mgCu · dm^{-3} (Table 1) and were about five times lower than the threshold set for surface waters [24].

Copper is a biogenic element and in water reservoirs is to be found in the form assimilable by organisms. It is necessary for plants to grow. At a concentration higher than 0.1 mg · dm^{-3} it hinders growth of aquatic plants, which is not a problem in the pond under study. The element is also very toxic to fish [18, 25]. The most harmful Cu compounds include Cu salt solutions and copper(II) hydroxide $Cu(OH)_2$, which forms an insoluble deposit. It may accumulate on fish gills and may cause fish to die [26]. Its toxicity largely depends on water hardness and pH. Copper toxicity is diminished by complexing substances [27]. Copper excess in water is highly toxic to biological activity, which in turn adversely affects self-purification [28]. According to Liebmann [18], copper is toxic to fish at concentrations of 80–800 μg · dm^{-3} and hinders self-purification at a concentration as low as 10 μgCu · dm^{-3}. The average content of the element found in the water was 0.0053 mgCu · dm^{-3} (Table 1) and as such does not pose any threat to aquatic organisms [18].

The copper concentration in the Park soil in 2000, as given by Karczewska et al [15], was 40–570 mgCu · kg^{-1}. The figures determined by the study in question were lower (Table 2) and almost like in the Selenga River sediments [22] mostly lower then in bottom sediments from estuary in Argentina [23].

According to the bottom sediments classification based on geochemical criteria, in terms of copper content the sediments in question belong to purity class I, because there was less than 20 mgCu · kg^{-1} of the metal in them, whereas the sediments from sites 7 and 8 in the autumn meet the requirements for purity class II (> 20 mgCu · kg^{-1}) [19].

The average annual rate of Cu accumulation in bottom sediments was calculated at $1.5 \cdot 10^{-3}$.

The water in the pond may be classified as belonging to surface water purity class I, as none of the cadmium concentrations recorded throughout the year exceeded 0.005 mgCd · dm^{-3} [18]. Most probably cadmium mainly occurs as CdS and $CdCO_3$, although in surface waters it may also be found as Cd^{2+} ion or it may form complexes $[Cd(OH)]^+$, $[CdCO_3]^0$, $[CdSO_4]^0$ and [CdCl].

According to Liebmann [18], cadmium is toxic to fish at concentrations of 3–20 mg · dm^{-3} and it hinders self-purification at 0.1 mg · dm^{-3}. In the pond examined the mean concentration of the metal amounted to 0.0008 mg · dm^{-3}, *ie* it was much lower that the threshold value quoted as harmful to fish [18].

The average cadmium concentration in the water was the lowest out of all the remaining metals covered by the study (Table 1).

Cadmium content in the bottom sediments of the pond covered by the study was much lower (Table 2) than that quoted by Dojlido [18], as 0.100 mgCd $\cdot$ kg^{-1} to over 3.000 mgCd $\cdot$ kg^{-1}.

According to the bottom sediments classification based on geochemical criteria, in terms of cadmium content the sediments in question belong to purity class I, because at none of the sampling sites did the concentration exceed 1 mgCd $\cdot$ kg^{-1}.

Tests done by PIOS in 2007 [29] covering 125 lakes showed that the arithmetic mean of the metal amounted to 0.8 mgCd $\cdot$ kg^{-1}. In a 2008–2009 study done on the pond, which had 8 sampling sites, the arithmetic mean of Cd was by 50 % lower than that calculated for the lakes [18]. The concentration of Cd in bottom sediments was lower then bottom sediment from Dubai creek 3.83–7.20 mgCd $\cdot$ kg^{-1} [20] and like in bottom sediments of Black Sea [21] mostly lower then in bottom sediments from estuary in Argentina [23]. In 2000 Karczewska et al [15] determined that cadmium concentration in soil was from 0.05 to 4.5 mgCd $\cdot$ kg^{-1}. In a 2005 study by Licznar et al [30] cadmium concentration in the humus fell within the range of 0.2–1.0 mg Cd $\cdot$ kg^{-1} [15, 16].

Gardiner claims that the cadmium accumulation rate ranges from $5 \cdot 10^3$ to $50 \cdot 10^3$ [18]. Cadmium does not remain long in water and precipitates as carbonates or is absorbed by suspensions and bottom sediments. In the study concerning the problem the accumulation annual rate amounted to nearly $0.5 \cdot 10^3$, *ie* was much lower than the figures given by Gardiner [18].

Cadmium was the metal with the lowest concentration both in water and in the bottom sediments. Its accumulation rate was also the lowest when compared with the other metals.

Lead at higher concentrations is toxic to fish. It accumulates in the food chain, in the liver and the kidneys. Toxicity to fish is acute at concentrations of 200–10 000 μg $\cdot$ dm^{-3}. According to Harrison [18], acute toxicity to fish is observed at concentrations ranging from 100 to 15 000 μg $\cdot$ dm^{-3}. Lead concentration in the pond water was below the range given above (Table 1).

The soil had much more of lead than the sediments. The low content of the element may have been caused by two factors: a significant number of trees and bushes in the park, which captured the metal very effectively and did not allow it to permeate from the nearby roads to the water, and by leaching of the metal by the water over the bottom sediments. Lead content in the park's soil in 2000 ranged from 60.0 to 435.0 mgPb $\cdot$ kg^{-1} [15]. A 2005 study by Licznar et al [28] showed that its concentration in the humus oscillated between 39.5 and 202.0 mgPb $\cdot$ kg^{-1} [15, 16].

Because at none of the sampling sites did the concentration of Pb-toxic metal exceed 50 mgPb $\cdot$ kg^{-1}, according to the bottom sediments classification based on geochemical criteria, the sediments in question belong to purity class I [19]. The tests of 125 lakes done by PIOS in 2007 showed that the arithmetic mean lead concentration in them amounted to 37 mgPb $\cdot$ kg^{-1} [29]. The pond analysis conducted in 2008/2009 at 8 sampling sites showed a concentration seven times smaller than that in the lakes (Table 2). The concentration of lead was lower then in bottom sediment from Dubai creek 35.75–53.50 mgPb · kg^{-1} [20] and in bottom sediments of Black Sea [21] but almost like in the Selenga River sediments [22] mostly lower then in bottom sediments from estuary in Argentina [23].

The average annual lead accumulation rate in the bottom sediments in the Szczytnicki Park pond amounted to $1.3 \cdot 10^3$, and was 1000 times smaller than that in Ontario Lake (1.4–3.0). The accumulation rate of the element oscillates between $0.1 \cdot 10^3$ and $1 \cdot 10^3$ [18], *ie* it is higher in the sediments studied, as it amounted to $1.5 \cdot 10^3$.

According to Liebmann [18], nickel at concentrations of 25–50 mgNi · dm^{-3} has a toxic effect on fish and at 0.1 mgNi · dm^{-3} it hinders self-purification. The obtained results indicated that the element posed no threat to fish [18]. Nickel concentration in water of the Szczytnicki pond (Table 1) may be affected by its leaching from soil [31].

Nickel had the highest average annual rate of accumulation in the bottom sediments, amounting to $2.8 \cdot 10^3$. The lowest nickel concentrations were measured in the autumn and winter, oscillating around 5.0 mgNi · kg^{-1} (Table 2).

In 2008/2009 the arithmetic mean nickel concentration at 8 sampling sites on the pond was over 7 mgNi · kg^{-1} dry mass, *ie* it was similar to that established in the 2007 PIOS study [29]. The concentration of lead was lower then in bottom sediment from Dubai creek [20] and in bottom sediments of Black Sea [21].

A statistically material correlation ($p < 0.05$) between the content in the sediments of Zn and Cu, Ni, Pb and between Cd and Ni was found.

Conclusions

The water and bottom sediments in Szczytnicki Park should be regarded as unpolluted with metals.

The accumulation rates of the studied metals in the sediments should be ordered as follows: Ni > Cu > Zn > Pb > Cd.

The metal concentrations in the sediments should be ordered differently: Zn > Cu > Ni > Pb > Cd

Pb and Cd had the lowest accumulation rates and concentrations in the bottom sediments. The order of the average concentrations of the studied metals in the water (except for Pb) corresponds to that of their contents in the bottom sediments.

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KUMULACJA WYBRANYCH METALI W OSADACH DENNYCH STAWU W PARKU SZCZYTNICKIM WE WROCŁAWIU

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Uniwersytet Przyrodniczy we Wrocławiu

Abstrakt: Celem pracy była ocena stopnia zanieczyszczenia wody i osadów dennych oraz ocena stopnia kumulacji wybranych metali (ołów, kadm, cynk, miedź, nikiel) w osadach dennych stawu położonego w Parku Szczytnickim. Próbki do badań pobrano z 8 stanowisk, czterokrotnie podczas roku: wiosna (24 IV 2008), lato (19 VII 2008), jesień (18 XI 2008), zima (10 II 2009). W wodzie oznaczono: temperaturę, odczyn, twardość ogólną oraz stężenie metali (Zn, Cu, Cd, Pb, Ni). W osadach dennych analizowano zawartość oraz kumulacje powyżej podanych metali. Współczynniki kumulacji badanych metali w osadach dennych uszeregowane są w sposób następujący: Ni > Cu > Zn > Pb > Cd, natomiast szereg stężeń tych metali w osadzie dennym wygląda następująco: Zn > Cu > Ni > Pb > Cd. Najniższe współczynniki kumulacji i najniższą zawartość w osadzie dennym stwierdzono dla ołowiu i kadmu. Badana woda oraz osady denne należały do niezanieczyszczonych metalami.

Słowa kluczowe: ołów, kadm, cynk, miedź, nikiel, osady denne, kumulacja, staw Szczytnicki

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INFLUENCE OF THE INHOMOGENEOUS SOILS PROPERTIES ON THE DIFFERENCE BETWEEN APPARENT AND ACTUAL THICKNESS OF LNAPL

WPŁYW WŁAŚCIWOŚCI GRUNTÓW NIEHOMOGENNYCH NA RÓŻNICĘ MIĘDZY MIĄŻSZOŚCIĄ POZORNĄ I RZECZYWISTĄ LNAPL

Abstract: The paper presents the results of laboratory experiments conducted with use of the inhomogeneous soils. The focus of these experiments was to investigate if the hydraulic conductivity plays an important role in the case of such soils. Another aim of the research was to investigate the influence of the coefficient of graining non-uniformity and the effective grain size on the difference between apparent and actual thicknesses. The obtained results indicate that the hydraulic conductivity influences the difference between apparent and actual thickness of LNAPL in the case of inhomogeneous soils. The results confirmed that the product of the hydraulic conductivity of soil and the coefficient of graining non-uniformity can play an important role in the model describing the relationship between apparent and actual thickness of LNAPL on the groundwater table.

Keywords: LNAPL, actual thickness, apparent thickness, hydraulic conductivity, coefficient of graining non-uniformity, effective grain size

The *light non-aqueous phase liquids* (LNAPL) infiltrating into the subsurface from underground storage tanks, pipelines and cisterns pose a threat to soil and groundwater [1–4]. If the layer of LNAPL floats on the groundwater table the initial remediation step should be its recovery [1, 2, 5]. In order to a proper design of this operation an assessment of the contamination plume volume is required. To assess this volume observation wells are commonly installed in the contaminated porous medium to measure the thickness of LNAPL layer [1]. However, the actual LNAPL thickness (the thickness on the groundwater table) is different from the apparent thickness (the thickness observed in the monitoring well) [5–7]. This difference depends on the properties of soil and the amount and properties of LNAPL released to the soil [6,

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8–10]. A number of methods exist for estimating the actual thickness from the apparent thickness data, but the results obtained with different formulas are inconsistent, and in many cases inaccurate [6, 11].

The results of laboratory investigations conducted previously with use of homogeneous soils [9] indicate that the appropriate model for estimating the actual LNAPL thickness should include the properties of soil and LNAPL. The results show that the key parameter of soil is hydraulic conductivity and the important parameters of LNAPL are the density and dynamical viscosity. An additional important parameter that depends on properties of both: soil and LNAPL is the soil permeability of LNAPL [9].

The goal of this paper was to investigate if the hydraulic conductivity can play an important role in the model of relationship between apparent and actual thicknesses in the case of the inhomogeneous soils. Another aim of the research was to examine the influence of the coefficient of graining non-uniformity and the effective grain size of the inhomogeneous soils on the difference between apparent and actual thicknesses.

Materials and methods

The laboratory experiments were carried out in 10 cm diameter Plexiglas columns with filter-tubes as monitoring wells (Fig. 1).

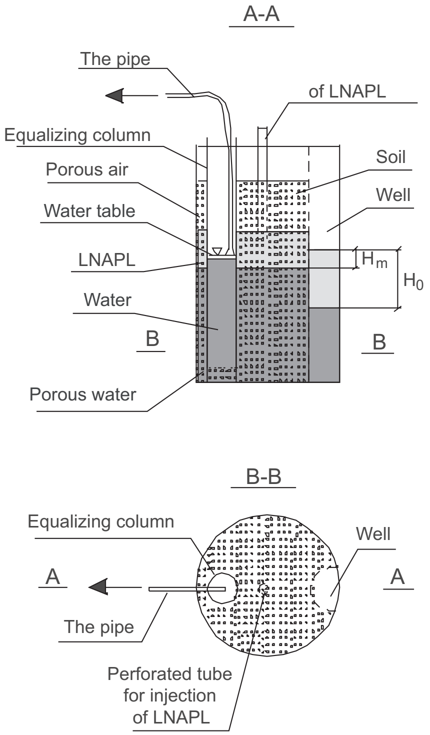

Fig. 1. The experimental column

The experiments were performed with use of four model soils (Table 1) and one type of LNAPL – the rape oil (Table 2).

Table 1

Properties of soils used in the experiments

Soil	Effective grain size d_{10} [mm]	Hydraulic conductivity at 10 ^{o}C k_{10} [m/d]	Coefficient of graining non-uniformity U [-]
1	0.19	$1.12 \cdot 10^{1}$	2.53
2	0.17	$1.04 \cdot 10^{1}$	2.18
3	0.33	$3.46 \cdot 10^{1}$	1.64
4	0.18	$0.78 \cdot 10^{1}$	1.56

Table 2

Properties of LNAPLs used in the experiments (at temperature of 20 ^{o}C)

Type of LNAPL	Density ρ_o [kg/m^3]	Specific gravity γ_o [N/m^3]	Dynamical viscosity η_o [kg/m·s]
Rape oil	918	9005.58	0.07

In each experimental column was inbuilt the equalizing column with perforated bottom. The columns were packed with the soil samples (soils 1–4) and filled with tap water until the water table reached the assumed elevation. After 3–4 days first rations (about 100 cm^3) of diverse LNAPLs, coloured with the pigment – Sudan III, were injected directly above the capillary fringe zone. After subsequent 3–4 days, the apparent and actual LNAPL thicknesses were measured in the well and in soil. The actual thickness was the distance between LNAPL-water interface in the soil and air-LNAPL interface in the well (without the capillary fringe of LNAPL in the soil). This procedure was repeated at least 10 times. The water table in each equalizing column was kept constant during experiments. The top of each experimental column was protected against LNAPL evaporation by the cover.

Results and discussion

On the base of results of laboratory experiments the point graphs were plotted, which show the relationships between apparent and actual thicknesses of LNAPL (Fig. 2). The previous findings show that such relationships are approximately linear [6, 11]. For each plot the linear trend line was fitted. The obtained values of R-squared coefficient were high (R^2 = 0.8428–0.93) in each case.

On the base of the obtained equations (see Fig. 2) the apparent thicknesses were derived for actual thicknesses equal to 5 cm. Next the differences between apparent and actual thickness were calculated (Table 3).

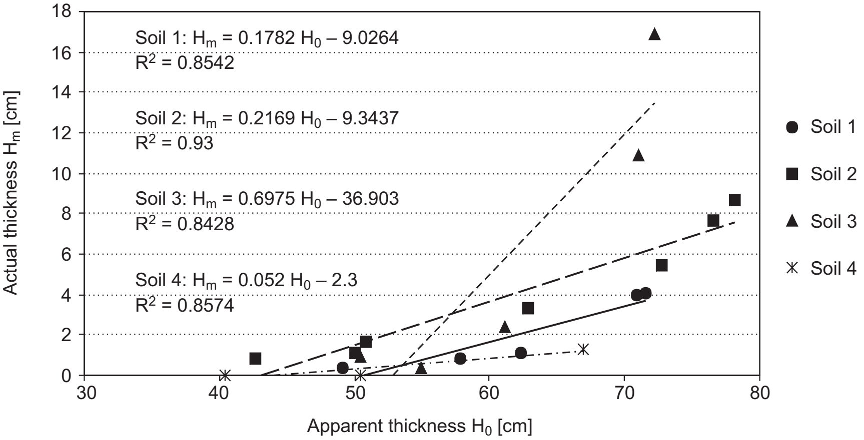

Fig. 2. The relationships between apparent and actual thicknesses for soils 1–4

Table 3

Differences between apparent and actual LNAPL thicknesses at actual thicknesses of 5 cm for soils 1–4

Soil	Actual thickness H_m [cm]	Apparent thickness H_0 [cm]	Difference between thicknesses $H_0 - H_m$ [cm]
Soil 1	5	78.71	73.71
Soil 2	5	66.13	61.13
Soil 3	5	60.08	55.08
Soil 4	5	140.38	135.38

Fig. 3–6 show the influences of selected properties of soils 1–4 on the difference between apparent and actual thicknesses. The graph in the Fig. 3 shows the influence of

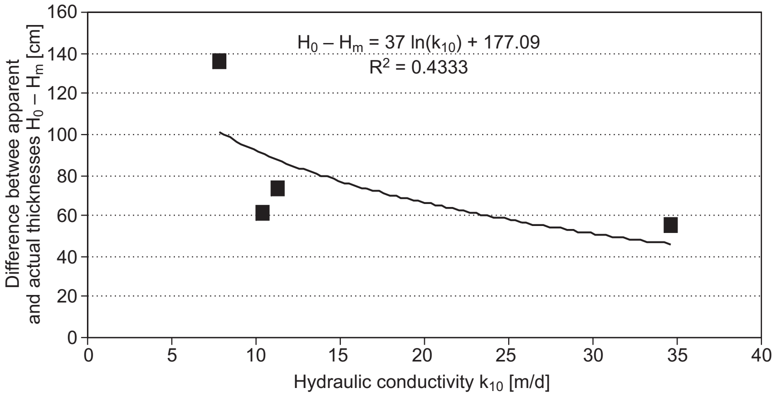

Fig. 3. The influence of the hydraulic conductivity on the difference between apparent and actual thicknesses for soils 1–4

the hydraulic conductivity at 10 °C (k_{10}) on this difference. The logarithmic trend line was fitted for the graph. The value of R-squared coefficient is in this case moderate ($R^2 = 0.4333$). It means that the hydraulic conductivity influences moderately the difference between apparent and actual thicknesses.

Figure 4 shows the influence of the effective grain size (d_{10}) on the difference between apparent and actual thicknesses. The linear trend line was fitted for this graph. The value of R-squared coefficient is in this case low ($R^2 = 0.2086$). This value suggests that the effective grain size influences narrowly the difference between apparent and actual thicknesses.

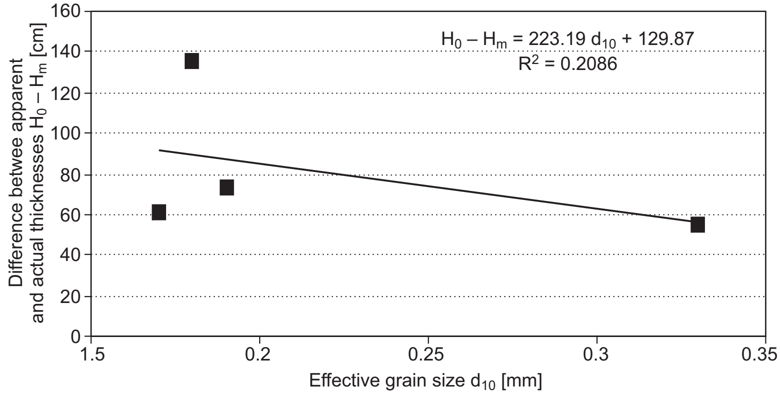

Fig. 4. The influence of the effective grain size on the difference between apparent and actual thicknesses for soils 1–4

Figure 5 shows the influence of the coefficient of graining non-uniformity of soil (U) on the difference between apparent and actual thicknesses. In this case the linear trend line was fitted for the graph. The value of R-squared coefficient is in this case low

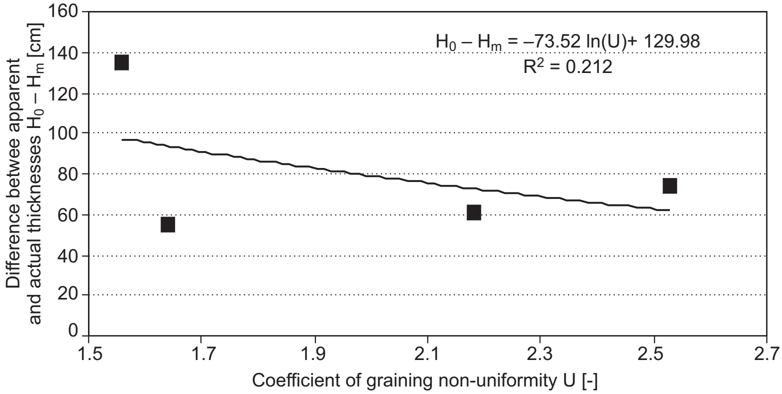

Fig. 5. The influence of the coefficient of graining non-uniformity of soil on the difference between apparent and actual thicknesses for soils 1–4

($R^2 = 0.212$). This value suggests that the coefficient of graining non-uniformity of soil influences narrowly the difference between apparent and actual thicknesses.

The graph presented in the Fig. 6 shows the influence of the product of the hydraulic conductivity and the coefficient of graining non-uniformity of soil ($k_{10} \cdot U$) on the difference between apparent and actual thicknesses. In this case the logarithmic trend line was fitted for the graph. The value of R-squared coefficient is in this case quite high ($R^2 = 0.7154$). This value suggests that this product ($k_{10} \cdot U$) influences considerably the difference between apparent and actual thicknesses.

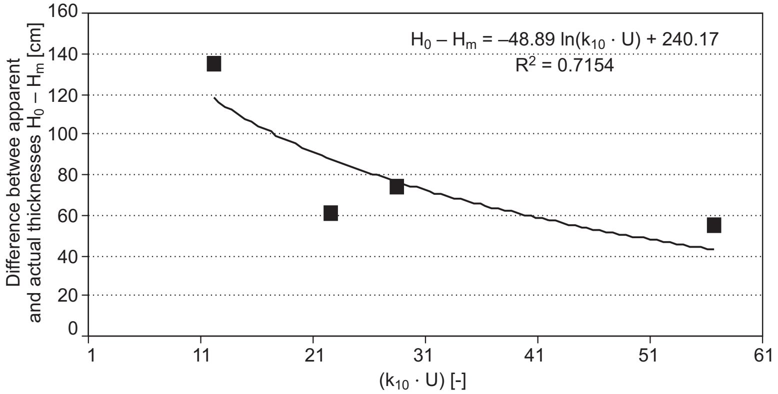

Fig. 6. The influence of the product of the hydraulic conductivity and the coefficient of graining non-uniformity of soil on the difference between apparent and actual thicknesses for soils 1–4

Conclusions

1. The results of laboratory experiments conducted with use of inhomogeneous soils show that the hydraulic conductivity has an impact on the difference between apparent and actual thicknesses, but it is not the only one parameter that influences this difference.

2. When the effective grain size increases, the difference between apparent and actual thicknesses decreases narrowly. The obtained value of R-squared coefficient is in this case low. It means that the effective grain size of soil can not play a significant role in the model of relationship between apparent and actual thicknesses.

3. The results confirm that the coefficient of graining non-uniformity does not influence significantly the difference between apparent and actual thicknesses. On the base of linear trend line it is observed the narrowly decrease of the difference between apparent and actual thicknesses with the increase of the value of graining non-uniformity of soil.

4. The results of the investigations show that the product of the hydraulic conductivity and the coefficient of graining non-uniformity of soil considerably influences the difference between apparent and actual thicknesses. This parameter can

play a significant role in the model of relationship between apparent and actual thicknesses in the case of the inhomogeneous soils.

Acknowledgements

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WPŁYW WŁAŚCIWOŚCI GRUNTÓW NIEHOMOGENNYCH NA RÓŻNICĘ MIĘDZY MIĄŻSZOŚCIĄ POZORNĄ I RZECZYWISTĄ LNAPL

Instytut Inżynierii Środowiska
Politechnika Częstochowska

Abstrakt: W niniejszym artykule zaprezentowano wyniki badań prowadzonych z zastosowaniem gruntów niehomogennych. Badania miały na celu sprawdzenie, czy w przypadku tego typu gruntów wartość współczynnika filtracji ma wpływ na różnicę między miąższością pozorną i rzeczywistą LNAPL. Przeanalizowano także znaczenie innych parametrów, takich jak średnica miarodajna i współczynnik nierównomierności uziarnienia. Na podstawie wyników badań laboratoryjnych ustalono, że współczynnik filtracji gruntu może mieć wpływ na obserwowaną różnicę między miąższością pozorną i rzeczywistą LNAPL w przypadku gruntów niehomogennych, zbliżonych do rzeczywistych. Zauważono również, że iloczyn współczynnika filtracji gruntu i współczynnika nierównomierności uziarnienia może odgrywać znaczącą rolę w modelu zależności między miąższością pozorną i rzeczywistą LNAPL na zwierciadle wody podziemnej.

Słowa kluczowe: LNAPL, miąższość rzeczywista, miąższość pozorna, współczynnik filtracji, współczynnik nierównomierności uziarnienia, średnica miarodajna

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EFFECT OF HIGH TEMPERATURE IN THE FLOWERING PERIOD ON GROWTH, DEVELOPMENT AND YIELDING OF FABA BEAN (*Vicia faba* L. spp. *minor*)

WPŁYW WYSOKIEJ TEMPERATURY W OKRESIE KWITNIENIA NA WZROST, ROZWÓJ I PLONOWANIE BOBIKU (*Vicia faba* L. spp. *minor*)

Abstract: The research was conducted in the growth chambers and in a greenhouse of Institute of Soil Science and Plant Cultivation – State Research Institute in Pulawy. Faba bean var. Nadwislanski was cultivated in Mitscherlich pots. An experimental factor was air temperature during flowering: optimal and higher. After flowering pots with plants were transferred from growth chambers to the greenhouse where they stayed up to full maturity. Too high temperature at flowering caused decrease of leaf area, leaf greenness index, plant height and changed the course of some phenological phases of faba bean. High temperature decreased yield which resulted from a lower number of pods per plant, number of seeds per pod and a lower mass of a thousand seeds.

Keywords: faba bean, high temperature, flowering, plant development, leaf area, yielding

Legumes are characterized by very large dependence on the course of weather conditions. This consequence is greater than yielding variability in the years of some other crop species [1]. Availability of water conditioned by the amount of precipitations and irrigation is a factor which in the greatest degree influences the size of seed yields obtained by this plant group. Legumes are particularly sensitive to water shortage in the soil at two phenological phases: at germination – emergence and at flowering [2]. Various genotypes of each species show different sensitivity to periodic water deficit in the soil [3, 4]. However, in some years there is observed a considerable reduction of seed yield in spite of sufficient water supply in plants. It can be supposed, therefore that temperature, as another important weather factor, has probably a restrictive effect on the

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level of obtained seed yield. This is all the more so as these observations concerned the years in which air temperature during flowering considerably exceeded values of means from many years. In attainable literature there is only some papers with results of experiments concerning studies on the response of a particular legume plant species to high temperature during flowering [5–8]. Most often it possible to find this information in relation to wheat [9–11], maize [12] or oilseed rape [13–14].

The aim of the present research was evaluation of the effect of high temperature in the flowering period on growth, development and yielding of faba bean.

Material and methods

Research was conducted at growth chambers and in a greenhouse of the Institute of Soil Science and Plant Cultivation – State Research Institute in Pulawy, in Mitscherlich pots contained mixture of soil and sand in the amount of 5 and 2 kg, respectively. The soil in the pots was slightly loamy sand with pH_{KCl} 4.8 and granulometric composition of 76, 16 and 8 %, for sand, silt and silt and clay, respectively. An experimental factor was air temperature in the period of flowering and pod setting: optimal (14 ^{o}C – night, 24 ^{o}C – day) and higher (18 ^{o}C – night, 30 ^{o}C – day). Relative air humidity at growth chambers was 85 %, and lighting 300 mikromol $\cdot$ m^{-2} $\cdot$ s^{-1}. Ten seeds of faba bean var. Nadwislanski were sowed to every pot, and after emergence plants were thinned to 5 at each pot. Plants in the experiment were fertilized with the following NPK doses (g $\cdot$ pot^{-1}): 0.1 N, 1.1 P and 1.4 K. Fertilizers were applied in a liquid form during plant watering at two terms: after emergence and at stage of 1–2 leaves. Moisture of soil during the vegetation was kept on the level 60 % of field water capacity. In the beginning of flowering plants were placed in growth chambers. After the end of this phase pots with plants were transferred to a greenhouse where stayed up to full maturity. Detailed observation of growth and plant development were conducted in the vegetation period. At green pod stage (BBCH 80) the measurement of leaf area was done by using leaf area measurer AM 300 (ADC BioScientific Ltd., UK) and measurements of SPAD index were performed with using Minolta Chlorophyll Meter SPAD-502. Values of SPAD units were measured on the first, second and third, fully developed leaf, counting from the top of a plant. Every measurement of SPAD index was a mean from 30 measurements performed on each plant. Just before the harvest of the plants, the measurement of their height was made and during the harvest the yield of particular faba bean organs as well as the following features of its structure were estimated: number of pods and number of seeds per plant, number of seeds per pod, a thousand seed mass and seed moisture content. Results of the research expressed as a mean from 3 pots were worked out statistically by using analysis of variance with the help of Tukey's confidence interval at the significance level $\alpha = 0.05$.

Results and discussion

The emergence of plants occurred after 9 days from sowing. Faba bean seeds were characterized by germination capacity on the level 95 %, so it was possible to obtain very good emergence which was measured as the number of seedlings per pot. Seedlings were characterized by good forming and big vigor. Faba bean plants grew from these seedlings produced a great mass of vegetative organs at initial stage of development. Placing the plants during flowering period in high temperature caused significant reduction of leaf area, decrease of leaf greenness and height of plants (Table 1).

Table 1

Mean values of chosen features of faba bean plants

Air temperature	Green pod [BBCH 80]		Full maturity [BBCH 90]
	Leaf area [cm^2 per plant]	Leaf greenness index [SPAD]	Height of plants [m]
Optimal	628^{b*}	584^{b}	1.12^{b}
High	514^{a}	445^{a}	0.97^{a}

* Numbers in columns denoted with the same letters do not differ significantly.

The same changes caused by higher temperature were found in case of lupine and barley [8]. Previous studies showed that thermal stress appearing in flowering period significantly restricts plant leaf area size as result of enhanced leaf senescence at conditions of higher temperature [6, 8, 15]. It was observed also that heat stress reduces chlorophyll content what was explained as effect of enzyme inhibition in this conditions [16]. In the case of faba bean, as legume plant, probably occurred disturbed supplying with nitrogen because high temperature affects nitrogen fixation [17]. Furthermore, in our experiment was observed a change the course of some developmental phases. The plants which at flowering grew in higher temperature conditions considerably earlier ended flowering and started pod setting as well as ripened about 3–4 days earlier than the plants cultivated at optimal air temperature. Mian et al [18] also observed changes of developmental phases of wheat caused by high air temperature. According to Rahman et al [15] higher temperature enhances plant growth and forces the maturity, so different growth and development stages occur earlier compared with optimal temperature.

Thermal conditions had also an effect on dry matter yield accumulated by particular organs of plants (Fig. 1). High temperature during plant flowering influenced negatively the size of vegetative and generative organs yield, while positively affected root mass. The decrease of the dry mass yield of faba bean which was grown during flowering at higher temperature was: 25.2, 32.5, 28.3 and 34.8 %, for stems, leaves, siliques and seeds, respectively, while the increase of roots dry mass yield was 10.3 %.

Roots play an important role in plant adaptation to high temperature by their significance in water and nutrient uptake, as well as their involvement in hormone synthesis affecting shoot growth and development [19]. However, physiological processes that are essential for root growth include carbohydrate metabolism. Maintaining high carbon-use efficiency at high temperatures is of fundamental importance, because roots depend solely on shoots for the supply of assimilates. Carbon supply to roots typically decreases while root respiratory carbon consumption of assimilates increases at high temperatures. So, excessive consumption of assimilates for the

Fig. 1. Yield of dry matter of faba bean plant organs at full maturity

maintenance of roots may be a significant factor limiting plant productivity, particularly under stressful environments [20]. It is in accordance with studies of Lahti et al [21], who found that in the higher temperature treatment, carbon allocation to root growth may have been favored at the expense of shoot growth.

The results of experiments with pea, lupine and barley [6, 8] demonstrate that a short period of thermal stress causes aboveground biomass yield reduction in consequence of photosynthetic productivity decrease. Photosynthesis is closely related to plant growth and crop yields, and photosystem II (PS II) is considered as the most heat-sensitive component of the photosynthetic apparatus [22]. As an effect of higher temperature was observed the decrease of transpiration and stomatal conductance values [8]. According to Yan et al [22] photosynthesis is mainly limited by stomatal conductance and reduced transpiration led to increase in leaf temperature and subsequent negative effects on photosynthesis. The studies of Podlesny and Podlesna [8] and Rahman et al [15] showed that the final biomass and grain yield of wheat and lupine-barley mixture significantly decreased in high compared with optimal temperature.

The main indicator of plant productivity is seed yield which is depended on genotype and different stresses during vegetation period. At our studies was found the negative effect of higher air temperature conditions on faba bean seed yield and its structure features (Table 2). The decline of the seed yield was caused by decreasing of the pod number per plant and the number of seeds per pod as well as a lower mass of a thousand seeds.

Table 2

Mean values of faba bean yield structure

Air temperature	Full maturity [BBCH 90]			
	number of pods per plant	number of seeds per pod	number of seeds per plant	weight of 1000 seeds [g]
Optimal	4.2^{b*}	3.3^{b}	13.9^{b}	382^{b}
High	3.3^{a}	2.1^{a}	8.9^{a}	337^{a}

* Numbers in columns denoted with the same letters do not differ significantly.

Research by other authors also prove the negative effect of high temperatures during flowering on generative development of plants, which in consequence, is a reduction of size and yield quality as well as yield structure features [6, 10, 12]. The negative effect of high temperature is probably, the disturbance of assimilates transport and, most of all, changes of direction of its distribution which decreases of their export to flowering branches and fruit [23]. The periods of flowering and seed set are clearly critical stages for exposure to heat stress. Development of male (pollen, anthers) and female (stigma, ovary) parts are the most sensitive organs to abiotic stress in reproductive biology [17]. So, high temperature effects at flowering are related to another development, pollen sterility and pollen production what reduce pollen germination. According to Porch and Jahn [24] pollen sterility is one of the key factors limiting legume yield under high temperature. Therefore flower abortion is caused by male sterility resulting from abnormal pollen development. Studies of Rahman et al [15] showed that high temperature may effects the pollen viability and fertilization and thereby reduce the number of set fruit and developed seeds. Individual seed weight which is considered as one of the major yield components is also significantly influenced by higher temperature because it enhances plant maturation causing reduction in seed growth duration which ultimately resulted in smaller seeds.

Conclusion

1. Too high temperature at flowering caused reduction of leaf area and decrease of plants height as well as changed the course of some phenological phases of faba bean.
2. Plants which grew at higher temperature conditions considerably earlier ended flowering and started pod setting and ripened a few days earlier than plants cultivated at optimal air temperature.
3. High temperature at flowering negatively influenced on yield of vegetative and generative faba bean organs, limited in the greatest degree the size of seed yield.
4. Decline of faba bean seed yield at higher air temperature conditions was a consequence of a lower number of pods per plant, a lower number of seeds per pod and weaker filling of seeds.

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WPŁYW WYSOKIEJ TEMPERATURY W OKRESIE KWITNIENIA NA WZROST, ROZWÓJ I PLONOWANIE BOBIKU (*Vicia faba* L. spp. *minor*)

[1] Zakład Uprawy Roślin Pastewnych, [2] Zakład Żywienia Roślin i Nawożenia
Instytut Uprawy Nawożenia i Gleboznawstwa
Państwowy Instytut Badawczy w Puławach

Abstrakt: Celem podjętych badań było określenie wpływu wysokiej temperatury w okresie kwitnienia i zawiązywania strąków na wzrost, rozwój i plonowanie zróżnicowanych genotypów bobiku. Badania prowadzono w fitotronach oraz w hali wegetacyjnej Instytutu Uprawy Nawożenia i Gleboznawstwa – Państwowego Instytutu Badawczego w Puławach, w wazonach Mitscherlicha zawierających mieszaninę 5 kg ziemi ogrodowej i 2 kg piasku. Wysiewano bobik odmiany Nadwiślański. Czynnikiem doświadczenia była temperatura powietrza w okresie kwitnienia: optymalna (noc: 14 °C, dzień: 24 °C) oraz podwyższona (noc: 18 °C, dzień: 30 °C). Następnie wazony z roślinami przeniesiono do hali wegetacyjnej i utrzymywano je do dojrzałości pełnej. Przez cały okres wegetacji utrzymywano wilgotność gleby na poziomie 60 % ppw. Zbyt wysoka temperatura w okresie kwitnienia powodowała redukcję powierzchni liściowej i zmniejszenie wysokości roślin oraz zmianę przebiegu niektórych faz fenologicznych bobiku. Rośliny, które przetrzymywane były w warunkach podwyższonej temperatury, znacznie wcześniej kończyły kwitnienie i rozpoczynały zawiązywanie strąków oraz dojrzewały o kilka dni wcześniej niż rośliny rosnące w optymalnej dla bobiku temperaturze powietrza. Wysoka temperatura zmniejszała plon co było konsekwencją mniejszej liczby strąków na roślinie i liczby nasion w strąku oraz istotnego zmniejszenia masy 1000 nasion.

Słowa kluczowe: bobik, wysoka temperatura, rozwój roślin, powierzchnia liści, plonowanie

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IONIC LIQUIDS FOR THE EXTRACTION OF *N*-BUTANOL FROM AQUEOUS SOLUTIONS

CIECZE JONOWE W EKSTRAKCJI *N*-BUTANOLU Z ROZTWORÓW WODNYCH

Abstract: The article describes the extraction of *n*-butanol from four-component aqueous solutions, also containing acetone and ethanol. All of these three chemicals are the main constituents of the so-called fermentation broth – a product of ABE (Acetone-Butanol-Ethanol) fermentation process. Nowadays, ABE fermentation, which is one of the oldest butanol production technologies, seems to be a viable alternative to petrochemical methods that have so far dominated the industry. Such considerations are driven by the steady depletion of fossil fuels, and thus, worldwide tendencies to use renewable resources instead, but also by the popularization of clean production and green chemistry principles. The physicochemical properties of biobutanol are very similar to that of gasoline and diesel fuel. Therefore, there exists a real potential for its widespread use as a fuel additive, if not a direct application in internal combustion engines. For that reason, the effective separation of biochemically derived butanol may have a great impact on fuel production technology, which is by far crude oil oriented. The main challenges of applying traditional solvents in liquid-liquid extraction are their toxicity and usually high volatility that prevents an economically justified partitioning of the extract components. Hence, there arises a growing interest in non-volatile, thermally stable and water immiscible ionic liquids. Properties of these new 'designer solvents' have not been fully recognized yet, but the full range of their possible applications may appear as unlimited. In this study, phase separation research has been made in five-component systems of water, acetone, butanol, ethanol and ionic liquid. Two different ionic liquids have been used: 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][Tf_2N]. Experimental results confirm the efficient recovery of *n*-butanol from aqueous solutions when volumes of both liquid phases are approximately equal.

Keywords: liquid-liquid extraction, ionic liquids, biobutanol, renewable resources

Introduction

Butanol is a chemical capable of numerous industrial and non-industrial applications, but, first and foremost, it should be considered as a viable alternative to gasoline. It

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displays favourable combustion characteristics and, as a fuel additive, it is superior to widely used ethanol in many aspects (*eg*, lower volatility, higher energy content, better miscibility with diesel fuel and gasoline). From a technical standpoint, appropriate modifications in the existing combustion engines are also possible [1]. Comparison of butanol with other fuels is shown in Table 1 [2, 3].

Table 1

Properties of fuels

Property	Butanol	Gasoline	Diesel fuel	Ethanol	Methanol
Energy density [MJ/dm^3]	**29.2**	**32.0**	35.9	19.6	16.0
Air-fuel ratio (AFR)	**11.2**	**14.7**	14.6	9.0	6.5
Heat of vaporization [MJ/kg]	**0.43**	**0.36**	0.23	0.92	1.20
Research Octane Number (RON)	**96**	**91–99**	—	129	136
Motor Octane Number (MON)	**78**	**81–89**	—	102	104

Since the 1950s butanol has been produced almost solely from fossil fuels. However, one of the oldest industrial biochemical techniques of butanol production, which has been superseded by crude oil processing, is the ABE fermentation exploiting certain types of anaerobic *Clostridium* bacteria. In view of the steady depletion of non-renewable resources and recent proecological regulations this method is certainly worth looking into again.

Of all the applicable bacterial species, the genetically modified strain *Clostridium beijerinckii* is the most butanol selective – the total concentration of products (*ie*, acetone, butanol and ethanol) obtained in the fermentation broth ranges between 15–26 g/dm^3 depending on the substrates, with butanol yield approaching 19–20 g/dm^3 [4].

Separation of biobutanol from the fermentation broth poses a complex technical problem. First of all, it must be carried out in a continuous manner, because an excessive concentration of products inhibits the bacteria [5, 6]. Secondly, the applied technique should not be demanding in terms of energy and costs. Finally, classical extraction solvents might be of practical use, but they are mostly toxic and volatile, in other words, not environmentally friendly.

A variety of methods have been proposed for the stated purpose, such as gas stripping, adsorption, *liquid-liquid extraction* (LLE), pervaporation and membrane solvent extraction. However, liquid-liquid extraction, along with pervaporation, appear to be the most suitable techniques [7]. Therefore, ionic liquids, which recently gained some notable recognition in science and industry, may turn out to be highly appropriate for the recovery of biobutanol.

Ionic liquids (ILs) are liquid substances composed solely of ions (in a general sense, molten salts). However, most salts melt in high temperatures. Therefore, contemporary ionic liquids are molten salts with a melting point below 100 ^{o}C [8]. There are also salts melting in temperatures lower than 20 ^{o}C and they are called *room-temperature ionic liquids* (RTILs). Ionic liquids are often described as *designer solvents*. Because of practically unlimited number of combinations between anions and cations, their properties may be “adjusted” to suit certain process requirements [9, 10].

The main attributes of ionic liquids making them useful in separation of mixtures are very low volatility and wide liquid range (often exceeding 200 °C) [11, 12], which may allow their relatively easy regeneration (via low pressure distillation) and recirculation. A lack of toxic fumes is the additional benefit.

It is of fundamental significance that the ionic liquid employed as the extracting solvent should be hydrophobic, *ie*, immiscible with the aqueous phase. It has been noted that some of the ILs are water-miscible while others are not, even if their chemical structures are not much different [13]. Nevertheless, hydrophobicity is the main quality determining the choice of ILs for this study.

Materials and methods

The study of phase equilibrium was conducted in five-component two-phase systems of water, acetone, butanol, ethanol and ionic liquid, corresponding to the fermentation broth composition. Acetone, butanol and ethanol used in the experiments were of at least 99 % purity (CHEMPUR, Poland). Two hydrophobic ionic liquids, 1-hexyl-3--methylimidazolium hexafluorophosphate [Hmim][PF_6] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [Bmim][Tf_2N] (IoLiTec, Germany), whose chemical structures are shown in Figs. 1 and 2, were applied as extractants.

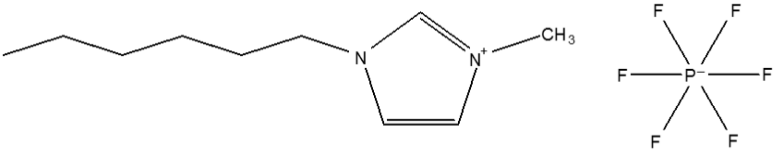

Fig. 1. Structural formula of 1-hexyl-3-methylimidazolium hexafluorophosphate

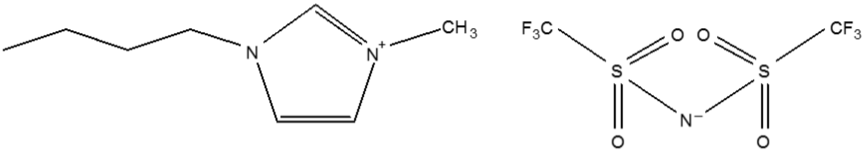

Fig. 2. Structural formula of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

The experiments were carried out with four-component feed solutions containing water, acetone, *n*-butanol and ethanol. Mass fractions of acetone, butanol and ethanol varied between 0 and 6 %. Volumes of solutions ranged from 0.5 to 2.0 cm^3. Approximately 1.0 cm^3 of ionic liquid was added to each feed solution. Then the mixtures were placed in a thermostated water bath and shaken for about 1.5–2.0 hrs. At the end of that period they were centrifuged to expedite phase separation (Fig. 3).

The extraction was conducted at temperatures of 10, 30 and 50 °C.

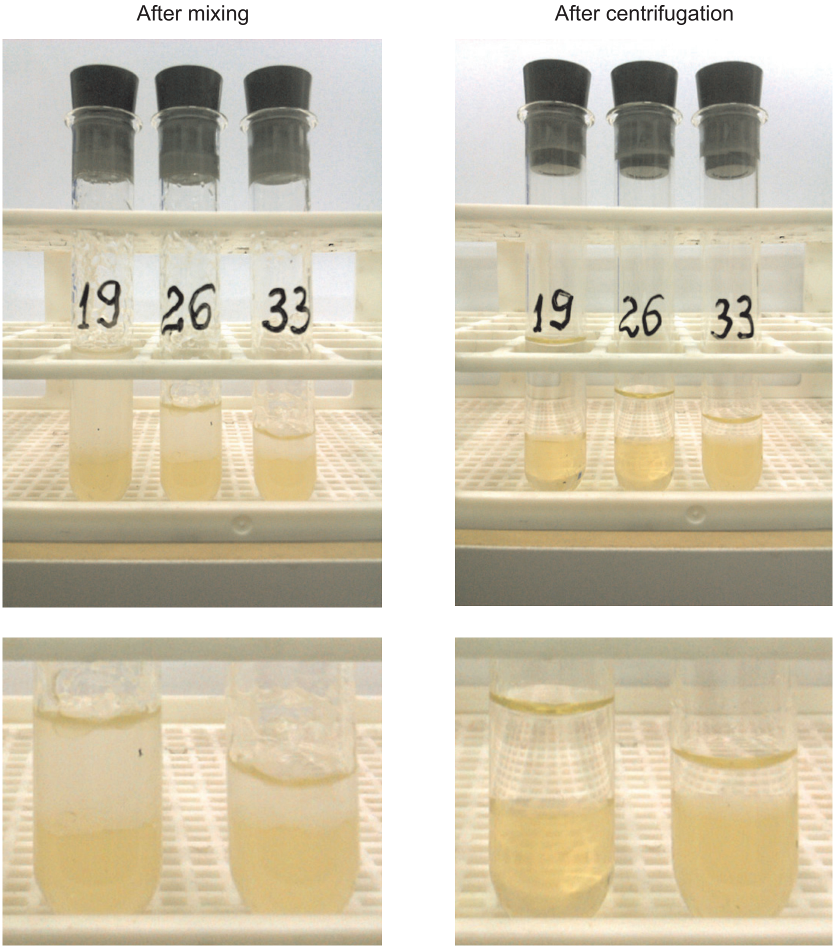

Fig. 3. Mixtures containing water, 1-hexyl-3-methylimidazolium hexafluorophosphate, acetone, butanol and ethanol

Concentrations of acetone, butanol and ethanol in the raffinate (water-rich phase) were measured with a gas chromatograph (TraceGC ThermoFinnigan with Quadrex Corp. column) using internal standard (methanol).

Water content in the extract (IL-rich phase) was determined by Karl-Fischer titration (Mettler Toledo T70 Titrator).

Measurements showed that the presence of solvents, especially butanol and acetone, as well as temperature augmented solubility of water in both ionic liquids. Likewise, solubility of ionic liquids in water was enhanced by the same factors.

ILs content in the raffinate was calculated based on a separate set of experiments, in which all mixture components, but ionic liquid, were evaporated.

Preliminary tests revealed that both ionic liquids were practically non-volatile at the boiling point of the highest boiling component of the mixture, in this case butanol

(BP = 116–118 °C). Therefore, ionic liquid was the only component that did not evaporate from the solution of known mass and content.

Complete compositions of both phases were calculated on the basis of the above mentioned measurements.

Results

Phase equilibrium of five-component systems has been described by distribution coefficients, extraction efficiency and selectivity defined as follows:

– Extraction efficiency

$$\eta = \left(1 - \frac{C_W}{C_F}\right) \cdot 100 \tag{1}$$

where: C_F – concentration of a component in the feed solution (aqueous phase) [g/g],
C_W – concentration of a component in the raffinate (water-rich phase) after separation [g/g].

– Distribution coefficient

$$\alpha = \frac{C_{IL}}{C_W} \tag{2}$$

where: C_{IL} – concentration of a component (also water) in the IL-rich phase after separation [g/g],
C_W – concentration of a component (also water) in the water-rich phase after separation [g/g].

– Selectivity

$$\beta = \frac{\alpha}{\alpha_W} \tag{3}$$

where: α – distribution coefficient of a component,
α_W – distribution coefficient of water.

Calculated distribution coefficients and selectivities are given in Tables 2 and 3, where m_{IL}/m_W is a mean ionic liquid and water mass ratio for a given set of experiments. This ratio's value results from the differences between densities of ILs and water. Assuming approximately equal volumes of both phases, the IL-rich phase is heavier. The experiments have been done with ca 0.5, 1.0 and 2.0 cm^3 volumes of aqueous solutions.

Table 2

Distribution coefficients and selectivity of [Hmim][PF_6]

Temperature [^{o}C]	m_{IL}/m_W	α_A	α_B	α_E	α_W	β_A	β_B	β_E
10.0	0.609	1.043	1.089	0.181	0.024	45.77	47.44	7.32
10.0	1.201	0.917	0.889	0.124	0.022	41.32	39.85	5.48
10.0	2.575	0.999	0.912	0.111	0.021	47.38	43.70	5.20
30.0	0.625	1.122	1.371	0.200	0.029	39.43	43.92	7.01
30.0	1.219	1.110	1.242	0.162	0.027	41.14	47.23	6.03
30.0	2.478	1.081	1.178	0.169	0.025	43.84	46.16	6.91
50.0	0.601	1.269	1.808	0.237	0.033	39.73	56.31	7.19
50.0	1.206	1.176	1.546	0.214	0.031	38.85	50.63	6.99
50.0	2.475	1.205	1.492	0.190	0.027	45.68	56.67	7.15

Table 3

Distribution coefficients and selectivity of [Bmim][Tf_2N]

Temperature [^{o}C]	m_{IL}/m_W	α_A	α_B	α_E	α_W	β_A	β_B	β_E
10.0	0.789	0.907	1.153	0.145	0.023	40.62	51.04	6.28
10.0	1.574	1.065	1.330	0.154	0.022	48.45	60.54	7.02
10.0	3.140	0.935	1.247	0.124	0.021	45.02	60.31	5.96
30.0	0.787	1.124	1.695	0.215	0.028	39.50	59.05	7.57
30.0	1.570	1.037	1.516	0.192	0.027	39.00	56.37	7.25
30.0	3.154	1.040	1.464	0.169	0.024	43.76	61.56	7.06
50.0	0.789	1.167	2.053	0.257	0.034	35.77	62.61	7.73
50.0	1.578	1.097	1.869	0.228	0.031	36.03	61.12	7.44
50.0	3.165	1.249	1.970	0.239	0.027	46.87	74.31	8.96

Distribution coefficients of butanol are presented below in form of diagrams, where m_{IL}/m_W on the horizontal axis are overall mean ionic liquid and water mass ratios corresponding to each of the three different volumes of feed solutions (as noted above).

In general, rise in temperature causes the increase of distribution coefficients, and thus extraction efficiency, which is illustrated with the example of butanol in Figs. 4 and 5. At the same time, at constant temperatures distribution coefficients tend to diminish, or at least remain within quite a narrow range, when m_{IL}/m_W ratios are higher. Similar tendencies may be observed for acetone and ethanol. It is important to mention that both the accuracy and number of experiments that have been performed may be insufficient to draw unequivocal conclusions about the nature of these changes. Of course, very low distribution coefficients of water reflect its bad miscibility with ionic liquids used as extracting agents, in other words both ILs are strongly hydrophobic.

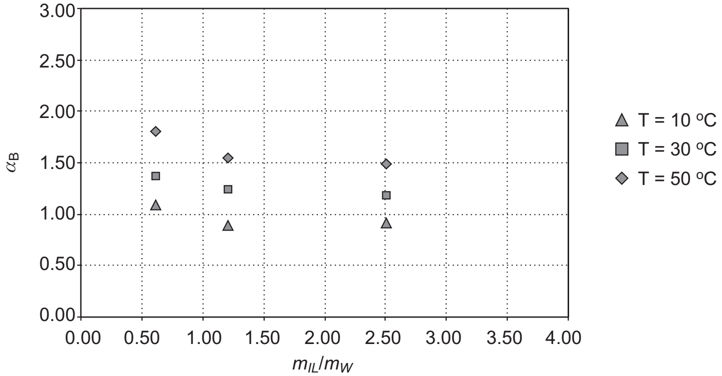

Fig. 4. Distibution coefficients of butanol after extraction by [Hmim][PF_6]

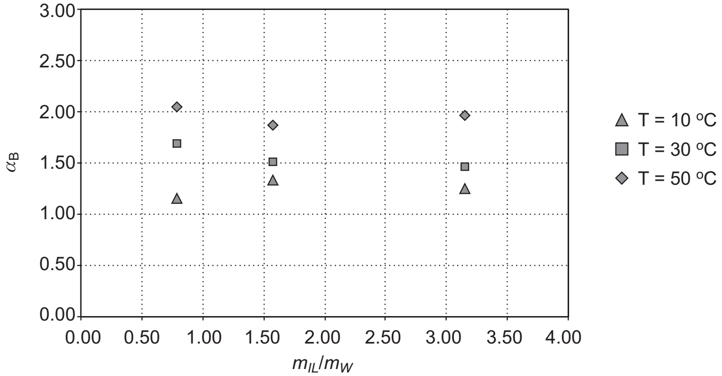

Fig. 5. Distibution coefficients of butanol after extraction by [Bmim][Tf_2N]

Selectivities, which are dependent on distribution coefficients, also show erratic behaviour. For butanol and perhaps ethanol they seem to grow with increasing temperature, but this relation is not visible in case of acetone. Both ionic liquids provide comparable selectivites for acetone (in the range of 35.0–50.0) and ethanol (in the range of 5.5–8.5), but [Bmim][Tf_2N] seems to be more butanol-selective than [Hmim][PF_6], especially at higher temperatures.

Comparisons of the extraction efficiencies are presented in Figs. 6–11.

As can be seen from the diagrams, [Bmim][Tf_2N], compared with [Hmim][PF_6], provides slightly better separation of all the three substances from aqueous solutions, but still the efficiency for ethanol is quite low. Under economically reasonable conditions, that is at room temperature and with volumes of ILs equal to the volumes of feed solutions, it does not exceed about 20 %. Under the same conditions separation efficiencies for acetone and butanol are much higher reaching up to ca. 55 % and 58 %, respectively after extraction by [Hmim][PF_6] and ca 60 % and 69 % after extraction by [Bmim][Tf_2N]. The highest efficiencies for all components have been obtained with

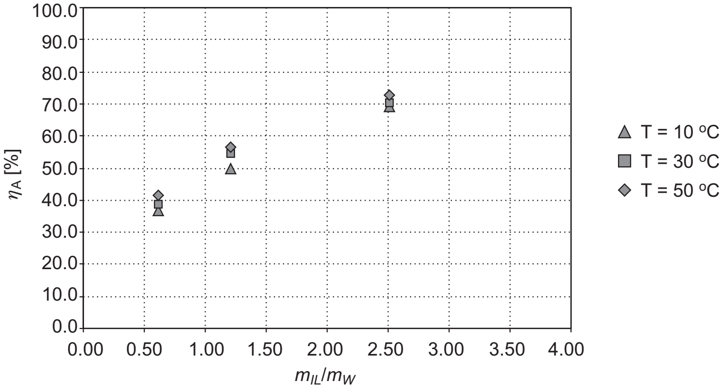

Fig. 6. Efficiency of acetone separation by [Hmim][PF_6]

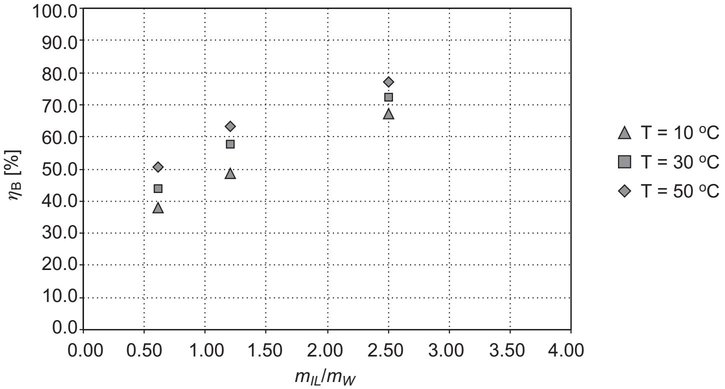

Fig. 7. Efficiency of butanol separation by [Hmim][PF_6]

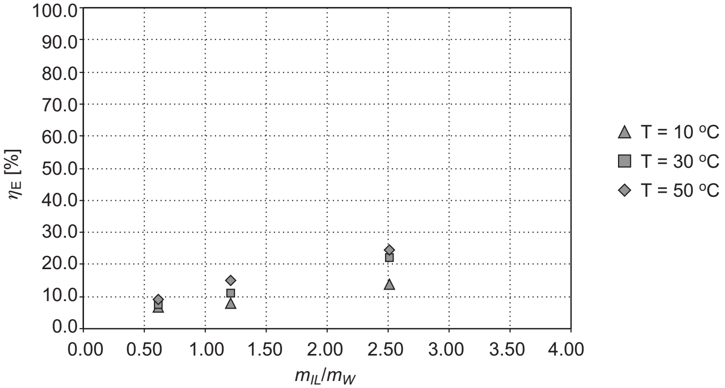

Fig. 8. Efficiency of ethanol separation by [Hmim][PF_6]

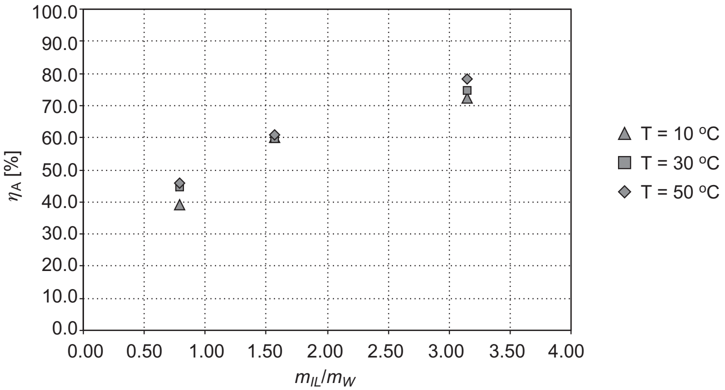

Fig. 9. Efficiency of acetone separation by [Bmim][Tf_2N]

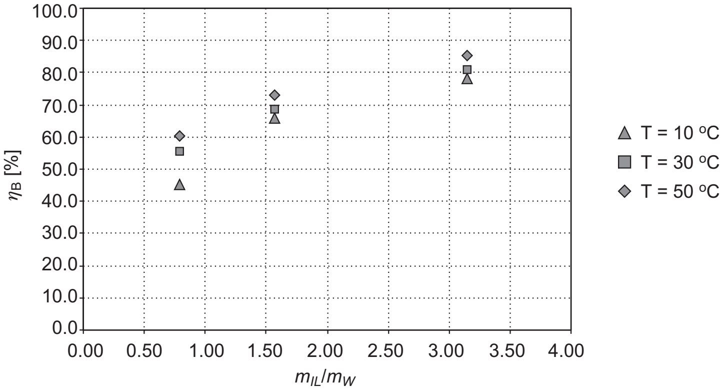

Fig. 10. Efficiency of butanol separation by [Bmim][Tf_2N]

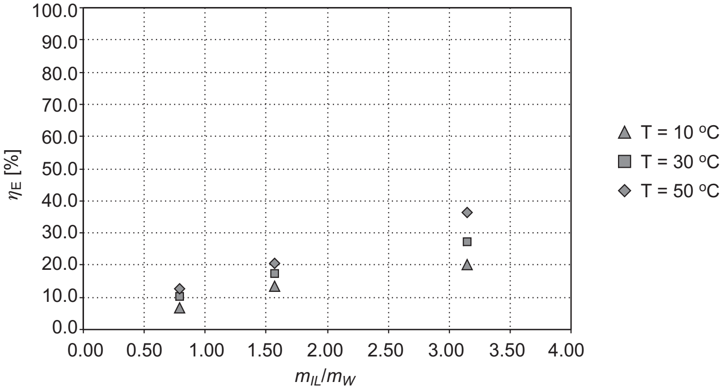

Fig. 11. Efficiency of ethanol separation by [Bmim][Tf_2N]

maximum relative volumes of ILs at 50 ^{o}C, the lowest efficiencies – with minimum relative volumes of ILs at 10 ^{o}C. Both of these factors, namely the amount of IL and temperature, influence the extraction process in the most significant way. However, the separation of butanol as well as ethanol seems to be more temperature-dependent than the separation of acetone.

Conclusions

From the results presented it is evident that there are two main factors having a decisive influence on the extraction efficiency, namely temperature and the amount of extractant. The highest efficiencies of butanol separation for both ILs studied, ca 77 % and 85 %, respectively, were reached at 50 ^{o}C with volumes of ILs approximately two-fold greater than volumes of feed solutions. Distribution coefficients for all substances essentially grow as temperature rises, but their variations resulting from different m_{IL}/m_W ratios at constant temperatures cannot be explained at this stage of the study. Also, an increase in temperature appears to favour separation of butanol over acetone and ethanol, which is reflected by growing selectivity (not so obvious for the other two substances). The extraction of butanol and ethanol seems to be more temperature-sensitive than the extraction of acetone, for which the efficiency relies mostly on the amount of extracting agent.

Generally speaking, both ionic liquids, when used in quantities comparable with the amount of feed solution, ensure about 50–65 % efficiency of extraction at room temperature for both acetone and butanol, which is of some significance from an energy consumption standpoint. At the same time, ethanol gets separated rather poorly. It is necessary to note that butanol, besides being the key product of ABE fermentation, has the strongest inhibitory effect on bacterial metabolism and, as such, needs to be removed from the fermentation broth in the first place. However, an excessive accumulation of by-products should also be prevented. Hence, further studies will be conducted to find ionic liquids most suitable for ABE extraction.

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CIECZE JONOWE W EKSTRAKCJI *N*-BUTANOLU Z ROZTWORÓW WODNYCH

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Abstrakt: Przedmiotem artykułu jest proces ekstrakcji *n*-butanolu z czteroskładnikowych roztworów wodnych zawierających ponadto aceton i etanol. Wymienione substancje są głównymi składnikami tzw. brzeczki fermentacyjnej stanowiącej produkt fermentacji ABE (acetonowo-butanolowo-etanolowej). Fermentacja ABE, jako jedna z najstarszych metod uzyskiwania biobutanolu stosowanych na skalę przemysłową, jest obecnie rozważana jako alternatywa dla dominujących w przemyśle procesów petrochemicznych. Znacząco przyczynia się ku temu perspektywa wyczerpania dostępnych zapasów paliw kopalnych, jak również podejmowane na szeroką skalę próby wdrażania zasad czystej produkcji i korzystania z odnawialnych źrodeł energii. Z uwagi na bardzo korzystne właściwości fizykochemiczne istnieją realne możliwości bezpośredniego zastosowania biobutanolu w silnikach spalinowych, bądź wykorzystania go jako dodatku do oleju napędowego i benzyny. Skuteczna separacja biobutanolu pozyskiwanego przy pomocy metod biochemicznych może mieć zatem ogromny wpływ na rozwój technologii produkcji paliw płynnych. Problemem przy stosowaniu klasycznych rozpuszczalników w ekstrakcji ciecz-ciecz jest często ich toksyczność, jak również wysoka lotność uniemożliwiająca opłacalny ekonomicznie rozdział ekstraktu. Dlatego też w kręgu zainteresowania pojawiają się niskolotne i stabilne termicznie ciecze jonowe nierozpuszczalne w roztworach wodnych. Właściwości cieczy jonowych jako substancji stosunkowo nowych nie są jeszcze dokładnie poznane, jednak z uwagi na szeroki wachlarz potencjalnych zastosowań budzą one coraz większe zainteresowanie, a możliwości ich „projektowania" mogą wydawać się nieograniczone. Przeprowadzono badania równowagi ekstrakcyjnej w układach zawierających wodę, aceton, butanol, etanol i ciecz jonową. Wykorzystano w tym celu dwie ciecze jonowe: heksafluorofosforan 1-heksylo-3-metyloimidazolu oraz bis(trifluorometylosulfonylo)imid 1-butylo-3-metyloimidazolu. Wyniki eksperymentów potwierdzają wysoką skuteczność procesu ekstrakcji *n*-butanolu przy zbliżonych objętościach roztworu surowego i ekstrahenta.

Słowa kluczowe: ekstrakcja ciecz-ciecz, ciecze jonowe, biobutanol, odnawialne źrodła energii

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QUANTITATIVE-QUALITATIVE ANALYSIS OF SEWAGE FOR THE NEWLY DESIGNED SANITARY SEWAGE SYSTEM

ANALIZA ILOŚCIOWO-JAKOŚCIOWA ŚCIEKÓW DLA NOWO PROJEKTOWANEJ KANALIZACJI SANITARNEJ

Abstract: A basic kind of engineering activity improving quality and comfort of citizens' life is maintenance of the suitable sanitary state. The above may result from suitable devices and buildings of sewage transport and treatment. The correctly designed sewer system assures the uninterrupted intake of sewage at the minimization of the negative impact on human health and the environment. The existing sewer systems are frequently extended for new lines causing the growth of the quantity and load of pollutions in sewage entering the *wastewater treatment plant* (WWTP). This paper shows the results of the quantitative-qualitative analysis of sanitary sewage from the newly designed sanitary sewage system in the west site of Rejowiec Fabryczny. Our analysis was conducted to determine the increase of the pollutants load entering the WWTP. The analysis was based on the pollutants load in average-twenty-four hours samples of raw sewage sampled in the screens chamber in mechanical-biological WWTP. The results of sewage qualitative analyses from the period of years 2008–2009 were adopted to our research. The pollutants loads in the newly designed network in the west of Rejowiec Fabrycznego were defined basing on the research of the inequality of the water demand in seven household. This analysis allowed the pollutants loads prediction in raw sewage inside the newly designed network of the sanitary sewage system. The proposed analysis demands validation permitting for confirmation of assumed simplifications.

Keywords: sanitary sewage, sewage quality, sanitary sewage system, sewage quantity

The quantity and quality of sewage originated from households mainly depends on personal habits and standard of households accessory. It is assessed that the largest loads of pollution are generated in the toilet bowls and the least – in the handbasins [1]. The load of pollution in sewage is often determined by its origin. The municipal, industry or agricultural wastewaters often need individual approach in the decontamina-

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tion process in regard of their specific composition [2]. The composition and the quantity of sewage entering the *wastewater treatment plant* (WWTP) are often modified by infiltration and coincidental water (rainwater, meltwater, groundwater) getting to the sewage system [3]. Moreover, physical and biochemical processes occurring in the system affect the quality of sewage entering the WWTP. The developing biomass of heterotrofic microorganisms causes the process of sewage self-purification, or loss of the pollution load in the WWTP inflow against the load getting to the system [4–6]. Thus, designing of a WWTP should be more often integrated with designing of a sewage system. These objects should be treated as a whole instead of individual objects, because the sewage decontamination process occurs as early as the stage of sewage transport in the system [7–11].

The quantitative-qualitative characteristic of sewage is a necessary element both at the stage of designing of new WWTP and during extending or modernization existing objects [12].

The aim of this work was to conduct the quantitative-qualitative analysis of the sewage flowing in the WWTP from five newly designed parts of the sanitary sewage system in Rejowiec Fabryczny, Poland and to show the quantitative-qualitative distribution of this sewage in the successive hours during a natural day.

Material and methods

Characteristics of research object

A newly designed sanitary sewage system in the west part of Rejowiec Fabryczny city was used as a research object, on the basis which the quantitative-qualitative analysis of the sewage was conducted. The system includes the regions of Chelmska, Dworcowa, Lubelska and Boczna streets and it contains 90 individual households.

The Rejowiec Fabryczny city is located in the south-east of Lublin province. Its area amounts about 14 square kilometers [13]. Nearly 5 thousand citizens live there and population density amounts 342 persons per square kilometer [14]. The length of the combined sewer in-service is equal to 9.3 kilometers and the length of connections – 2.0 kilometers, that denotes 85 % households conected the sewage system. Sewage from both, existing and newly designed sewers will flow into the mechanical and biological WWTP with efficiency 800 cubic meters per a natural day. The WWTP has been existing since 1991 and it was modernised in 2003 [13, 15].

The newly designed sanitary sewage system, used in the our studies, consists of 5 parts including main sewers and connections. Each part will be connected with the existing system. The designed sewer is going to be made of PVC SN 4 pipes, overall length 4085 m. There will be chambers made of PE (425 mm in diameter) and concrete chambers (1200 mm in diameter) as an accessory of the system. Details on quantitative and size parameters are presented in Table 1 [13].

Table 1

The characteristics of the newly designed sanitary sewage system in Rejowiec Fabryczny

No. of sewer part	System length *L* [m] / Number of segments [unit]			Number of chambers [unit]		Number of segments / chambers [unit]
	PVC 160 [mm]	PVC 200 [mm]	PVC 315 [mm]	PE 425 [mm]	Concrete 1200 [mm]	
1	71 / 7	588 / 21	985 / 23	22	30	51 / 52
2	37 / 3	69 / 3	—	5	2	6 / 7
3	154 / 10	825 / 28	257 / 12	32	19	50 /51
4	62 / 5	222 / 9	—	11	4	14 / 15
5	104 / 6	711 / 26	—	20	13	32 / 33

The route of newly designed gravity sanitary sewage system was determined by ground slopes and existing subterranean and aerial infrastructure [16]. Pipes will be assembled below ground freezing depth, which is equal to 1.0 m for the second climate zone [17]. The scheme displaying the structure of the system (part no. 4) is presented in Fig. 1.

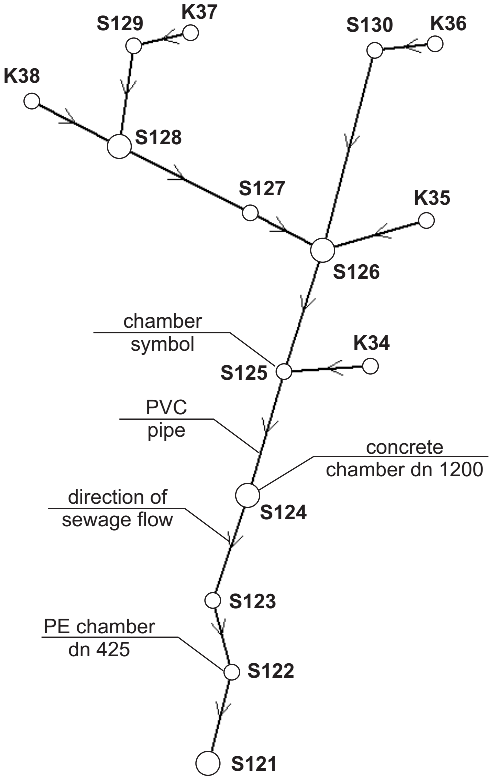

Fig. 1. Scheme displaying the structure of system (part no. 4)

Investigation method

The quantity of sewage flowing in the newly designed system was determined on the basis of average standards of water intake and number of citizens living in the area served by the new sewer.

It was assumed that 4 residents live in each household and the building is connected to a water supply system and there are toilet and bathroom and local source of hot water in the building.

On the basis of these assumptions the value of 100 $\text{dm}^3 \cdot \text{person}^{-1} \cdot \text{d}^{-1}$ was accepted as a the water intake standard [18]. Average quantity of sewage was calculated as:

$$Q_d^{śr} = q_j \cdot LM \tag{1}$$

where: q_j – unit daily quantity of sewage as a result of quantity of water consuming by one citizen [$\text{dm}^3 \cdot \text{person}^{-1} \cdot \text{d}^{-1}$], q_j = 80–100 $\text{dm}^3 \cdot \text{person}^{-1} \cdot \text{d}^{-1}$,

LM – number of citizens living in the area served by the new sewer [person].

Hourly and daily irregularity coefficients were assumed as $N_h = 2.0$ and $N_d = 3.0$, respectively, because the number of citizens is less than 5000 persons [19]. Maximal daily and hourly quantities of sewage were calculated taking into account daily and hourly irregularity of water intake:

$$Q_d^{\max} = Q_d^{śr} \cdot N_d \tag{2}$$

$$Q_h^{\max} = \frac{Q_d^{\max}}{24} \cdot N_h \tag{3}$$

where: N_d – daily irregularity coefficient of water intake [-],

N_h – hourly irregularity coefficient of water intake [-].

To provide for infiltration and case water maximal hourly quantity of the sewage from households was enlarged 25 %. On the basis of sewage quantity for particular segments of the system it was calculated the overall quantity of sewage flowing in the WWTP from the newly designed system as 11.25 $\text{m}^3 \cdot \text{h}^{-1}$. Details of calculations are presented in Table 2.

Analysis of sewage quality was conducted on the basis of results of investigation of raw sewage flowing in the WWTP accessible by courtesy of Zaklad Wodociagow i Kanalizacji in Rejowiec Fabryczny, conducted by Laboratorium Zakladu Inzynierii Srodowiskowej Eko-Projekt Sp. z o. o. Accessible results include analyses of sewage quality conducted in consecutive quarter of years 2008 and 2009. As parameters as BOD (*Biochemical Oxygen Demand*), COD (*Chemical Oxygen Demand*) and TSS (*Total Suspended Solids*) in average-day swage samples were tested. Results of analysis of sewage quality are presented in Table 3 (analysis according to [20–22]). Average pollutant load in raw sewage flowing in the WWTP was determined discounting the first measurement.

Table 2

The compilation of the sewage quantity from particular parts of the newly designed sewage system

No. of part	Citizens number, LM [person]	Sewage quantity				
		Unit daily, q_j [$\text{dm}^3 \cdot \text{person}^{-1} \cdot \text{d}^{-1}$]	Average daily, $Q_d^{avg.}$ [$\text{dm}^3 \cdot \text{d}^{-1}$]	Maximal daily, $Q_d^{\max}$ [$\text{dm}^3 \cdot \text{d}^{-1}$]	Maximal hourly, $Q_h^{\max}$ [$\text{dm}^3 \cdot \text{h}^{-1}$]	Maximal hourly, $Q_h^{\max}$ [$\text{dm}^3 \cdot \text{h}^{-1}$]
1	112	100	11200	22400	3500	3.50
2	16	100	1600	3200	500	0.50
3	120	100	12000	24000	3750	3.75
4	36	100	3600	7200	1125	1.13
5	76	100	7600	15200	2375	2.38
					Sum	11.25

Table 3

The quality of sewage flowing in the WWTP in years 2008 and 2009

No.	Quarter	Day	Sewage quality		
			BOD	COD	TSS
			[$\text{mg} \cdot \text{dm}^{-3}$]		
1	I	14.03.2008	95.7	200	40
2	II	19.06.2008	781	1660	1100
3	III	12.09.2008	388	1107	258
4	IV	12.12.2008	579	2283	994
5	I	01.04.2009	534	1503	560
6	II	16.06.2009	320	985	594
7	III	12.09.2009	511	1500	1070
8	IV	11.12.2009	345	1193	544
Average load determined discounting result of measurement in 1st quarter of year 2008			494	1462	731

To provide for irregularity of quantity and quality of sewage flowing in the WWTP, the sewage inflow pattern determined on the basis of water intake in seven selected households in consecutive hours during a day was used [15]. Measurement of quantity of water intake was made using household water-meter. Investigation was conducted in 2009. Obtained results of sewage inflow irregularity are presented in Table 4.

Quantitative irregularity of sewage inflow was determined multiplying maximal hourly quantity of sewage ($11.25 \text{ m}^3 \cdot \text{h}^{-1}$) by coefficient of inflow irregularity in consecutive hours of a day.

Table 4

Coefficients of irregularity of inflow of sewage to WWTP

Hour	Coefficient of sewage inflow irregularity [-]	Hour	Coefficient of sewage inflow irregularity [-]
1:00–2:00	0.02	13:00–14:00	0.25
2:00–3:00	0.00	14:00–15:00	0.38
3:00–4:00	0.00	15:00–16:00	0.61
4:00–5:00	0.00	16:00–17:00	0.34
5:00–6:00	0.00	17:00–18:00	0.22
6:00–7:00	0.38	18:00–19:00	0.15
7:00–8:00	0.45	19:00–20:00	0.37
8:00–9:00	0.35	20:00–21:00	1.00
9:00–10:00	0.42	21:00–22:00	0.67
10:00–11:00	0.33	22:00–23:00	0.59
11:00–12:00	0.33	23:00–24:00	0.51
12:00–13:00	0.23	24:00–1:00	0.06

Qualitative irregularity of sewage inflow was calculated multiplying average pollutant load determined on the basis of calculation presented in Table 3 by maximal hourly quantity of sewage, analogously to the method described by J. Adamek i K. Kudlik [23], taking into account coefficients of inflow irregularity (Table 4). Analysis was conducted treating all segments of newly designed sewer as one system, for which sewage quantity and pollutant load in consecutive hours of a day were determined.

Obtained results analysis

Calculations conducted for newly designed gravitational sanitary sewage system in the west part of Rejowiec Fabryczny enable maximal hourly quantity of sewage, average pollutant load and both quantitative and qualitative irregularity of inflowing sewage to be determined. It was established that maximal quantity of sewage flowing in the WWTP during an hour will be equal to 11.25 m^3 and average pollutant loads for this sewage will be as follow: BOD = 494 mg · dm^3, COD = 1462 mg · dm^3, TSS = 731 mg · dm^3. Distribution of quantitative inflow irregularity is presented in Fig. 2. Maximal quantity of sewage was observed at 8.00 p.m. Simultaneously, three other crests – at 7.00 a.m., 9.00 a.m. and 3.00 p.m. – were observed. The sewage flow for the mentioned hours amounted 5.06 $m^3 \cdot h^{-1}$, 4.73 $m^3 \cdot h^{-1}$ and 6.86 $m^3 \cdot h^{-1}$, respectively. Lack of WWTP inflow was observed at night between 2.00 a.m. and 5.00 a.m.

Distribution of pollutants load flowing in the WWTP in consecutive hours is presented in Fig. 3. Because qualitative pattern analogous to inflow pattern was used, the largest pollutant loads were obtained for an hour 8.00 p.m. Values of the pollutants were following then: BOD = 5.56 $kgO_2 \cdot h^{-1}$, COD = 16.44 $kgO_2 \cdot h^{-1}$, TSS = 8.23 $kgO_2 \cdot h^{-1}$. For the first crest for an hour 7.00 a.m. there was observed BOD = 2.50 $kgO_2 \cdot h^{-1}$, COD = 7.40 $kgO_2 \cdot h^{-1}$, TSS = 3.70 $kgO_2 \cdot h^{-1}$. For an hour 9.00 a.m. less values of pollutants concentrations were noticed: BOD = 2.33 $kgO_2 \cdot h^{-1}$, COD = 6.91

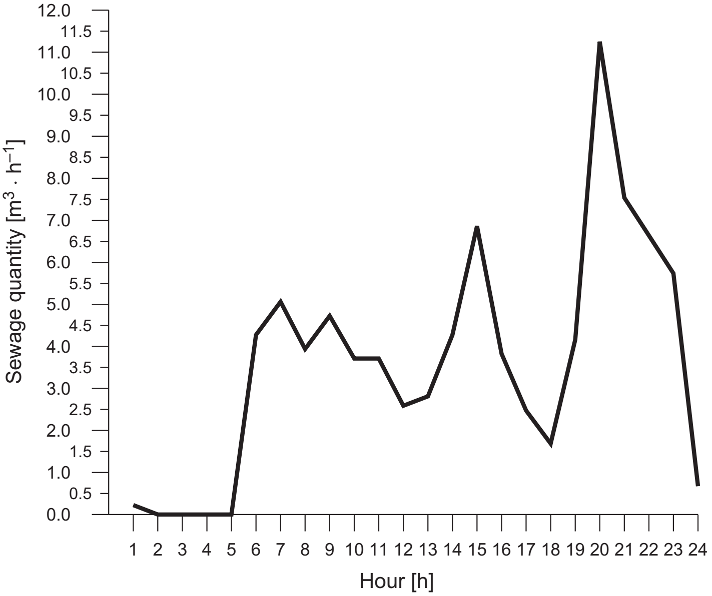

Fig. 2. The sewage quantity from the newly designed system running up to flowing in the WWTP

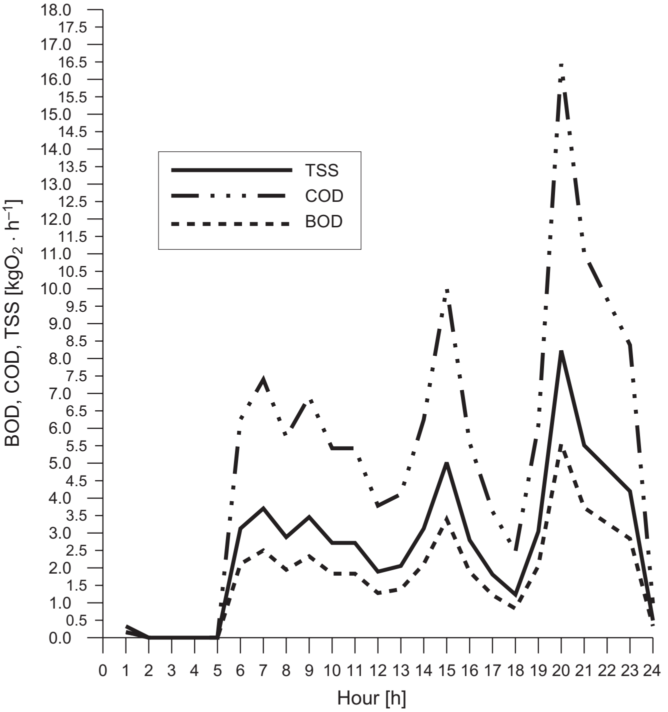

Fig. 3. Pollution load flowing in WWTP from newly designed sewage system

$kgO_2 \cdot h^{-1}$, TSS = 3.46 $kgO_2 \cdot h^{-1}$. In turn, larger values were observed for an hour 3.00 p.m.: BOD = 3.39 $kgO_2 \cdot h^{-1}$, COD = 10.03 $kgO_2 \cdot h^{-1}$, TSS = 5.02 $kgO_2 \cdot h^{-1}$. Analogously to qualititative distribution, there is not any changes in pollutant load between 2.00 a.m. and 5.00, because sewage does not flow in the WWTP in this time.

Conclusions

Results of conducted qualititative-quantitative analysis of sewage flowing in the WWTP from newly designed sanitary sewage system forecast both sewage quantity and pollutant load in row sewage flowing in the WWTP. They give a notion of a distribution of sewage quantity and pollutants concentration in consecutive hours of a natural day. They point out hours connected with quantitative-qualitative culmination of sewage in Rejowiec Fabryczny and display the time of lack of sewage flow in the WWTP. Thus, obtained results of the analysis enable operating, repairs, modernizations or possibly changes of sewage treatment technology to be better planned. Conducted analysis also improves that larger sewage flow after extending of the system in the city will not cause passing of maximal efficiency of the WWTP.

Simultaneously, the conducted analysis involves some errors, that can be caused by used simplifications and assumptions. Thus, its verification in real conditions is necessary to support accurateness of used patterns and assumed simplifications. Moreover, it is necessary to investigate that the pattern displaying irregulation of inflowing sewage quantity can be used to display irregulation of pollutants concentration in sewage.

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ANALIZA ILOŚCIOWO-JAKOŚCIOWA ŚCIEKÓW DLA NOWO PROJEKTOWANEJ KANALIZACJI SANITARNEJ W ZACHODNIEJ CZĘŚCI MIASTA RAJOWIEC FABRYCZNY

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Abstrakt: Podstawowym rodzajem aktywności inżynierskiej pozwalającym na poprawę jakości i komfortu życia mieszkańców jest utrzymanie odpowiedniego stanu sanitarnego. Możliwe jest to dzięki urządzeniom i budowlom pozwalającym na odprowadzanie i unieszkodliwianie ścieków. Prawidłowo zaprojektowana sieć kanalizacyjna zapewnia nieprzerwany odbiór ścieków przy minimalizacji negatywnego wpływu na zdrowie i środowisko naturalne. Coraz częściej istniejące już sieci kanalizacyjne są rozbudowywane, co powoduje wzrost ilości i ładunku zanieczyszczeń w ściekach dopływających do oczyszczalni. Niniejsza praca przedstawia wyniki analizy ilościowo-jakościowej ścieków sanitarnych z nowo projektowanej kanalizacji sanitarnej w zachodniej części miejscowości Rejowiec Fabryczny. Analiza miała na celu określenie wzrostu ładunku zanieczyszczeń dopływających do oczyszczalni. Przeprowadzono ją na podstawie analizy ładunku zanieczyszczeń w próbkach średnio-dobowych ścieków surowych, dopływających do kraty w istniejącej mechaniczno-biologicznej oczyszczalni ścieków. Do analizy przyjęto badania jakości ścieków z okresu 2008–2009, przeprowadzanych w kolejnych kwartałach. Ładunek zanieczyszczeń w kolejnych godzinach w ciągu doby z nowo projektowanej sieci w zachodniej części Rejowca Fabrycznego określono na podstawie badań nierównomierności rozbioru wody w siedmiu gospodarstwach domowych. Przeprowadzona analiza pozwala na określenie całkowitego prognozowanego ładunku zanieczyszczeń w ściekach surowych, doprowadzanego przez nowo projektowaną sieć kanalizacji sanitarnej. Jednocześnie określa ona ładunki dopływające w poszczególnych godzinach w ciągu doby. Zaproponowana analiza wymaga przeprowadzenia weryfikacji w celu potwierdzenia bądź odrzucenia prawidłowości zastosowanych uproszczeń.

Słowa kluczowe: ścieki sanitarne, jakość ścieków, kanalizacja sanitarna, ilość ścieków

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COMPUTATIONAL FLUID DYNAMICS MODELING OF BENZENE PROPAGATION IN WATER PIPE

OBLICZENIOWA MECHANIKA PŁYNÓW A MODELOWANIE JAKOŚCI WODY

Abstract: Modeling of water quality in distribution systems becomes nowadays a very popular tool applied in the processes of systems design and operation. Usually, according to everyday practice and literature reports, the chlorine propagation is one of the most frequently reported subjects of modeling. Meanwhile, literature presents many examples of pollutants originated in polymer pipes' material seriously deteriorating the quality of water in distribution systems. In this case, the *computational fluid dynamics* (CFD) may be applied to numerical calculations of simultaneous transport of several organic and non-organic pollutants in drinking water supply systems constructed of metal or polymer pipes. This paper contains the presentation of recognized pollutants migrating to drinking water from plastic pipes, possibilities of CFD application to water quality modeling and basic set of necessary input data as well as range of simulation results. The numerical calculations for dynamic benzene propagation inside the close loop pipe model was performed by Fluent, Ansys. Inc. for the three selected values of velocity flow. Our modeling attempt was performed as the preliminary step in the assessment of dynamic migration of pollutants originated from *high-density polyethylene* (HDPE) pipe and the input data and initial and boundary conditions were based on the available literature reports.

Keywords: water quality, numerical modeling, benzene, computational fluid dynamics, water supply systems

According to the rapid development of computing technologies and availability of various commercial and open source software, modeling of water quality flowing through the distribution systems has recently gained wide popularity among scientists, designers and operators of water supply systems. Numerical simulations focused on water quality modeling allow to predict the propagation of selected pollutant, or several pollutants simultaneously, along the whole system of drinking water distribution in various operational conditions. The modeled pollutants of different kinds may enter the water distribution systems in the source (*ie* disinfectants) or in any given point of distribution system, including wall reactions or migrations from pipe material [1]. Thus,

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modeling of contaminants transport helps to understand the movement and behavior of pollutants resulting in possibility of proper network planning and management.

The initial water quality, after processes of treatment and disinfection may be changed due to different causes leading to its deterioration – oxygen decay, disinfectant decay, the formation of disinfection by-products (*trihalomethanes*, THMs), change of color, smell and turbidity [2] as well as by leakage of organic or inorganic compounds from pipes materials during its contact with water [*eg* 3–5]. The strict regulations concerning the proper level of disinfectant cause the necessity of studies and monitoring of chlorine propagation and decay along the drinking water distribution systems – the decay of disinfectant agent may result in the degradation of microbial conditions of water supply network, causing thus a possible risk to the consumers' health [*eg* 6]. The recent literature studies show, however, that many different, organic and inorganic compounds creating possible danger to water quality (*eg* discoloration and fouling), customers complains as well as threats to public health may migrate from pipe material to drinking water during the distribution process through the water supply systems consisting of polymer pipes [*eg* 3–5, 7, 8] – *eg* metals and heavy metals, organotins compounds, volatile organic components (VOCs) or thermal stabilizers such as Irganox 10XX series. The mentioned problem becomes more serious due to the rapid increase of polymer pipes (PE, PVC) application to construction of water distribution systems. Recent reports show that plastic pipes make up over 50 % of all pipes installed worldwide [5]. In Poland approx. 70 % of newly constructed pipelines is made of polymer pipes [9]. The most popular recognized pollutants originated from polymer materials migrating to drinking water and influencing its quality and organoleptic properties [4, 8, 10–12] are presented in Table 1.

Table 1

The most popular recognized pollutants migrating to drinking water from plastic pipes

Metal stabilizers		Lead, organotins compounds, cadmium
Antioxidants		Irganox 1010, Irganox 1035, Irganox 1076, 2,6-di-tert-butyl-4-methyl phenol (BHT)
Products degradation of antioxidants used in polymer production		4-ethylphenol, 4-*t*-butylphenol,2,6-di-*t*-butyl-p-benzoquinone, 2,4-di-*t*-butylphenol,3,5-di-*t*-butyl-4-hydroxy styrene, 3,5-di-*t*-butyl-4-acetophenone, 3,5-di-*t*-butyl-4-hydroksy aceto phenone, 1,5-bis(*t*-butyl)-4-(2-carboxy-ethylidene)cyclohexa-1,4-dien-6-on, 3-(3,5-di-*t*-butyl-4-hydroksyphenyl)methyl propanoate, 3-(3,5-di-*t*-butylo-4-hydroksyphenyl)propanoic acid
VOCs	Esters	Butylacetate, Ethylhexanoate, Hexylacetate, Propylhexanoate, Butylhexanoate, Ethyloctanoate, Hexylhexanoate, Hexamethylbutanoate, Isobornylacetate, Ethyldecadienoate, 2,2,4-Trimethyl-1,3-2,2,4-TPD
	Aldehydes	Nonanal, Decanal
	Ketones	2-Decanon, 2-Undecanone, 2-Dodecanone
	Terpenoids	Alpha pinene, Delta carene, Limonene, Alpha terpinolene, Alpha farnesene
	Aromatic	Benzene, Toluene, Ethyl benzene, *m*- and *p*-Xylene, *o*-Xylene, Styrene, Isopropyl benzene, *n*-Propyl benzene, 1,3,5-Trimethyl benzene, 1,2,4-Trimethyl benzene, *p*-Isopropyl toluene, Naphthalene

Nowadays, the EPANET-based (by EPA, USA) chlorine propagation modeling, as the main disinfectant applied worldwide, is very popular and is being reported frequently [*eg* 13–20]. Usually, the following set of assumptions is required: distribution network is consisting of sources, pipes and nodes; flow directions in pipes are fixed, all hydraulic parameters and chlorine concentration in all outer sources are known [17]. Usually, the obtained results cover predicted chlorine concentrations in modeled systems nodes and pipes. However, these models have many disadvantages limiting the proper assessment of water quality in distributional systems (*eg* in some EPANET-based models propagation of studied pollutant may be studied only in system nodes) or just limiting their usage only to small networks as well as, which seems to be fairly important, simulating changes of narrow group of pollutants in fixed hydraulic conditions [2] – these may not be problematic for engineers and network operators but may be insufficient for more complicated hydraulic analyses.

Computational fluid dynamics and water quality modeling

More precise numerical calculations of water quality inside distribution systems covering different, not only chlorine, pollutants propagation in various, dynamic flow conditions (laminar or turbulent), chemical reactions inside the water body with different kinetic rates as well as migration of organic and non-organic compounds of pipe material to water are possible when *computational fluid dynamics* (CFD) methods are applied [*eg* 10, 21].

The development of CFD was started in the first two decades of XXth century and it has recently reached high popularity, due to the rapid development of computational techniques. CFD is now being applied in many branches of science and technology, from dynamic hydraulic of water supply and sanitation systems, water and wastewater treatment [22–24] to food industry [25], different technological processes [26], heating and ventilation [27, 28] and modeling of flow in rivers [29]. This popularity is reflected by availability of many open source and commercial CFD software.

One of the most popular commercial CFD software applied to water quality calculations is FLUENT developed by Fluent Inc., which was required by Ansys in 2006. Since then Fluent is a part of ANSYS engineering modeling software package. FLUENT was frequently reported as a successful tool in various simulation calculations of fluid flow [25, 29–32].

Fluid flow modeling in CFD is based on the following governing equations [*eg* 29, 33]:

– Conservation of mass:

$$\frac{\partial \rho}{\partial t} + div\, \rho \boldsymbol{u} = 0$$

– For incompressible fluid flow:

$$div\, \rho \boldsymbol{u} = 0$$

– Conservation of momentum:

$$\rho \frac{\partial u_i}{\partial t} + \rho u_j \frac{\partial u_i}{\partial x_j} = \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i$$

– Navier–Stokes:

$$\rho \frac{\partial u_i}{\partial t} + \rho u_j \frac{\partial u_i}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j}\left[\mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)\right] + \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i$$

where: ρ – fluid density,
t – time,
u – velocity,
$\boldsymbol{u}$ – velocity tensor,
τ_{ij} – stress tensor.

These equations, with the proper set of computational simplifications, boundary conditions and support of numeric techniques provide for comprehensive modeling tool for various laminar and turbulent, compressible and incompressible fluid, steady state and transient fluid (gas, liquid or multi-phase) flows analyses.

Qualitative calculations in CDF covering transport and mixing of reactive and non-reactive chemical species are usually based on the conservation equations of considered species. The mentioned equation general form for *i* species may be presented as follows [34]:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla(\rho \vec{u} Y_i) = -\nabla \vec{J}_i + R_i + S_i$$

where: Y_i – local mass fraction of *i* species,
$\vec{J}_i$ – vector of diffusion flux of species *i*,
R_i – production rate of *i* species by chemical reaction,
S_i – creation rate of *i* species by addition from dispersed phase or any other possible source.

Thus, the CDF calculations of multiple species transport and mixing in different flow conditions reflect convection, diffusion and reaction sources for each component species. The involved chemical reactions of transporting, mixing and migrating may occur in the bulk phase of fluid, on pipe/tank walls or particle surfaces as well as in porous media. So the most important advantages of CFD application to modeling of water quality in distribution networks should be now visible – the wide choice of pollutants, possibility of simultaneous calculations of multiple chemical processes occurring in water body and on pipe walls as well as in porous filtering bed, concentration of studied pollutants may be observed in any, freely selected, points of studied water system.

Usually, to apply CFD to engineering calculations the *finite element method* (FEM) or *finite volume method* (FVM) is required. Thus, the standard regime of the above-mentioned techniques are enabled: preparing the spatial mesh of finite elements/volumes and assignments of medium parameters, initial and boundary conditions in pre-processor, numerical calculations in model processor (solver) and results viewing and exporting in postprocessor. The appropriate skills represented by software users are required. Generally, CDF software is not suitable for beginners – some level of experience in computer modeling in FEM or FVM is necessary.

In Table 2, the exemplary necessary set of basic input data for flow and species transport-mixing model as well as the possible results of calculations by commercial software Ansys, Fluent [34] are presented.

Table 2

Input data and calculation results of CFD

Input data		Results
Material properties	Flow inputs	
Density, molecular weights, Viscosity, Mass diffusion coefficients – Fickian or full multi-component diffusion, User defined scalar diffusivity, isotropic or anisotropic	Flow type: laminar/turbulent, single or multiphase flow, turbulences model and its input data, Transport equations, Source and sink terms, Species transport type: mixing or non-mixing, species volumetric reactions, Constant or time and space dependant boundary conditions: inflow, outflow and wall: mass flow, pressure gradient or distribution, temperature, velocity distribution, species inlet mass fraction, wall surface reactions	Pressure and velocity of flow distribution, Mass and mole fraction of species, Concentrations and molar concentrations of species distribution, Laminar and effective diffusion coefficient of species, Kinetic and turbulent rate of reaction

Modeling assumptions

The numerical calculations of time-dependent benzene distribution inside the closed--loop pipe system was performed by Flunet, Ansys Inc. The developed modeled domain reflected the water body of 30 m long closed loop HDPE pipe of diameter 25 × 2.0 mm with internal surfaces absolute roughness assumed as $1 \cdot 10^{-6}$ m. The developed three--dimensional model consisted of 635112 nodes and 537959 elements, its volume was equal to 10.855 dm^3. Our modeling attempt contains several simplifications. The modeled movement of the whole water body with constant flow velocity was achieved by assigning the constant value of axial velocity to the selected small volume of fluid, transferring the movement to the rest of the model domain – our calculations were performed for three various values of water flow velocity magnitude: 0.5, 1.0 and 1.5 m/s (Reynolds number, respectively, 10445, 20900 and 31350). Time duration of our simulation covered 6 hours and was partitioned into 360 constant time steps of 60 s each.

Our modeling was performed for the turbulent flow of the viscous liquid, the realizable k-epsilon model of turbulences [35, 36] was adopted to our calculations. The following properties of water were assumed to modeling: density 998.2 kg/m^3, relative molecular mass 18.0152, dynamic viscosity 0.001003 kg/(m · s); while the benzene properties applied to numerical calculations were as follows: density 875.0 kg/m^3, relative molecular mass 78.11472 and coefficient of diffusion in water equal to $1 \cdot 10^{-9}$ m^2/s [10]. The initial benzene concentration was assumed to be equal to 0.0 g/dm^3. The boundary condition for benzene concentration applied to the outside boundary of the modeled domain (the outer surface of water body filling the studied HDPE pipe, border of the diffusive layer) was accepted as the concentration of benzene in water reported by Skjevark et al [4] equal to 500 ng/dm^3 ($5 \cdot 10^{-7}$ g/dm^3 which means the benzene *vs* water mass fraction in our model domain $5.01 \cdot 10^{-10}$).

Results and discussion

Analyzed results of our preliminary simulation of benzene migration and propagation inside the water body of closed loop covered mainly tested species distribution and time-dependent mean mass fraction and concentration for all three water flow velocities tested.

Figures 1–3 present the exemplary benzene distribution inside the selected part of the modeled domain – the pipe elbow.

Figure 1 shows the modeled distribution of benzene inside the selected part of the modeled water body. It is clearly visible that the distribution of the pollutant concentration depends to the water flow distribution inside the water stream – the locations of the highest benzene concentration zones are close to the pipe wall. The mean benzene mass fraction for the presented time step was equal to $1.859606 \cdot 10^{-10}$, which means $1.86 \cdot 10^{-7}$ g/dm^3.

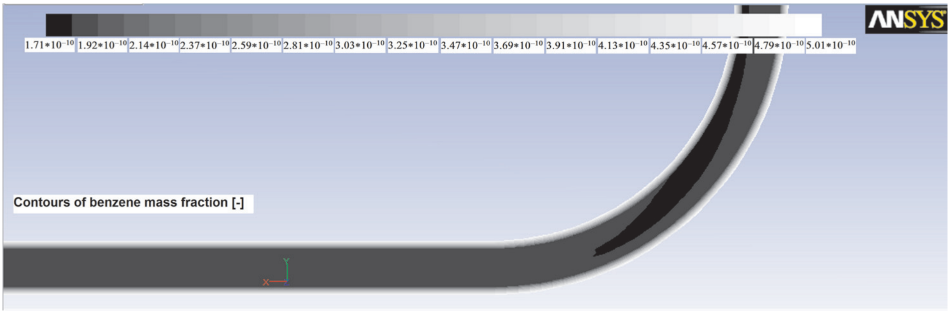

Fig. 1. The modeled benzene distribution inside water pipe: time duration 600s, mean flow velocity 0.5 m/s

The benzene distribution presented in Fig. 2, according to the higher flow velocity, shows higher values of the pollutant concentration and better mixing of benzene inside the water body. The mean benzene mass fraction for the presented time step was equal to $2.473962 \cdot 10^{-10}$, while its concentration was $2.47 \cdot 10^{-7}$ g/dm^3.

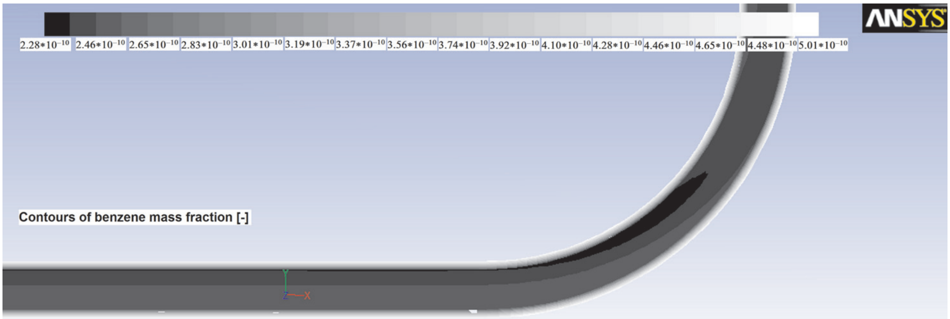

Fig. 2. The modeled benzene distribution inside water pipe: time duration 600s, mean flow velocity 1.0 m/s

Figure 3 presents the distribution of benzene concentration during the same time duration, 600s, but for the higher value of mean flow velocity, shows the highest concentrations of the tested pollutant and nearly total mixing of the pollutant inside the water stream. The mean benzene mass fraction for the presented time step was equal to $4.99121 \cdot 10^{-10}$, so its concentration in the modeled water body was equal to $4.98 \cdot 10^{-7}$ g/dm^3.

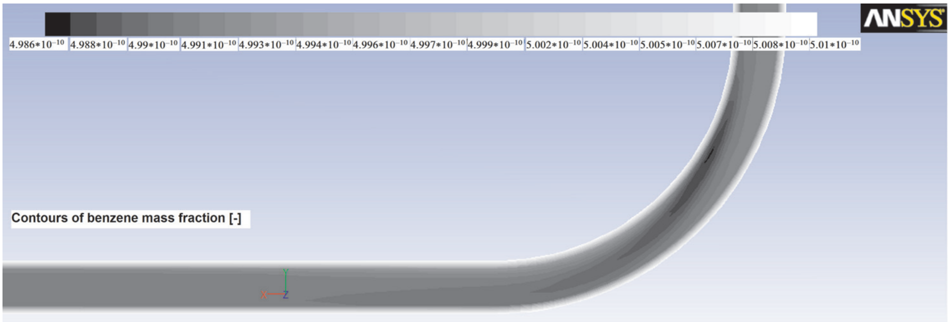

Fig. 3. The modeled benzene distribution inside water pipe: time duration 600s, mean flow velocity 1.5 m/s

Figure 4 presents the comparison of the results of all tested variants of benzene concentration modeling inside the close loop water body moving with the three various flow velocities: 0.5, 1.0 and finally 1.5 m/s.

Figure 4 shows that propagation ratio of benzene inside the flowing water stream of various flow velocity clearly depends to the flow speed and the Reynolds number. The higher flow velocity, the grater increase of the tested species concentration inside the water body. In all tested cases, the benzene concentration reaches the same, based on literature reports [4], maximum level, the accepted concentration equal to $5 \cdot 10^{-7}$ g/dm^3, assumed as the boundary condition, but in the different time. In case of flow velocity equal to 0.5 m/s the level of maximum concentration was achieved after 100 minutes, while it was observed 70 min. and 20 min. for 1.0 m/s and 1.5 m/s,

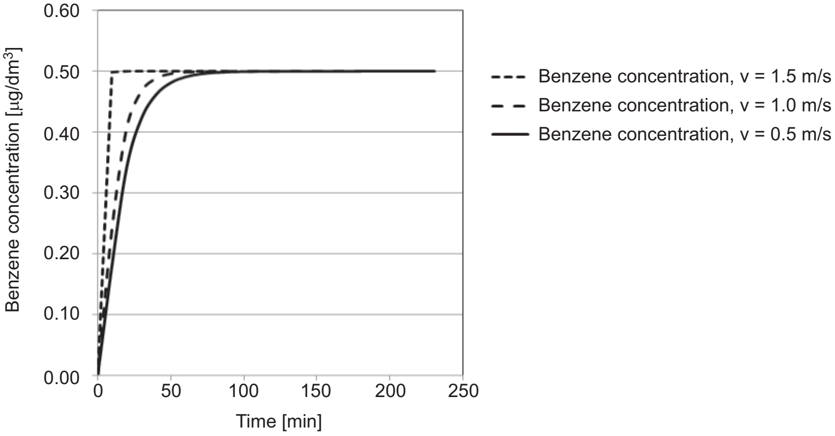

Fig. 4. Time-dependent modeled benzene concentration

respectively. It's shows the clear relation between the velocity of flow (as well as Reynolds number) and concentration of benzene in all tested cases. Moreover, the shape of curves presented in Fig. 4, showing the time-dependant concentration of BHT for various tested flow velocities, resembles the curves reported for the different pollutants migrating from pipe material to water, *eg butylated hydroxytoluene* (BHT) or *dibutyl tin* (DBT) [37, 38].

Summary and conclusions

The presented literature review shows a high potential of CFD application to water quality in distribution systems modeling. One may compute different scenarios, from the simplest ones (*eg* non-mixing transport of species in simple system) to the most complicated cases (*eg* mass transport of n-species with volumetric and wall surface reactions inside the complex distribution systems). The presented above advantages of CFD application allow numerical modeling of probably all engineering cases and problems encountered in practice. The popularity of CFD modeling among water distribution systems' designers and operators may be limited by its disadvantages: usually complex structure of open source software, high cost of commercial programs, required experience in data management and simulation calculations, high system and hardware requirements, full range of necessary input data (in dependence to the level of problem simplification). Nonetheless, the CFD's capabilities and range of possible application make it a worthy tool in modeling of water quality in distribution systems.

The presented preliminary modeling of dynamic, time-dependent benzene distribution inside the water body of closed loop water pipe, resultant from the migration of the pollutant from the HDPE pipe wall material to water, shows the good agreement with the concentrations of benzene in tap water reported in literature. Our calculations showed the clear relation between the calculated benzene concentration and velocity of flow and its Reynolds number – higher value of flow velocity (as well as Reynolds number) caused increased rate of benzene migration to the main zone of water stream resulting in quicker reaching the maximum observed concentration and more intensive mixing.

The next, planned step in development of our experiment is the laboratory experiment allowing to observe the process of benzene migration for HDPE pipe to water which would permit to adjust and validate our numerical modeling.

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OBLICZENIOWA MECHANIKA PŁYNÓW A MODELOWANIE JAKOŚCI WODY

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Abstrakt: Modelowanie parametrów jakości wody w systemach dystrybucji jest obecnie stosowane zarówno w procesie projektowania, jak i w eksploatacji sieci wodociągowych. Najczęściej stosowanym w modelowaniu wskaźnikiem jakości wody w sieci jest rozkład chloru. Badania literaturowe wskazują, iż istnieje duża grupa zanieczyszczeń pogarszających jakość wody a pochodzących z materiału przewodów. W celu numerycznego określenia transportu tych zanieczyszczeń w sieciach wodociągowych wykonanych z różnych materiałów może być zastosowana obliczeniowa dynamika płynów (CFD). W artykule przedstawiono najczęściej identyfikowane w wodzie zanieczyszczenia pochodzące z materiału przewodów wykonanych z tworzyw sztucznych, możliwości zastosowania CFD do modelowania jakości wody oraz niezbędne w tym celu dane wejściowe. Zaprezentowano numeryczne obliczenia rozprzestrzeniania się benzenu w wodzie wypełniającej układ zamknięty wykonany z przewodu HDPE. Obliczenia modelowe przeprowadzono za pomocą programu Fluent, Ansys Inc. dla trzech różnych prędkości przepływu przez modelowany przewód. Przedstawione obliczenia zostały wykonane jako wstępna ocena zachodzącej w warunkach dynamicznych migracji zanieczyszczeń organicznych z materiału rur HDPE, w związku z czym dane wejściowe oraz warunki początkowe i brzegowe ustalono na drodze badań literaturowych.

Słowa kluczowe: jakość wody, modelowanie numeryczne, benzen, obliczeniowa dynamika płynów, sieci wodociągowe

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ASSESSMENT OF POSSIBLE ZINC ACCUMULATION IN SOILS IN THE ZONE OF POTENTIAL ZINC-WORKS INFLUENCE

OCENA MOŻLIWOŚCI AKUMULACJI CYNKU W GLEBACH W STREFIE POTENCJALNEGO ODDZIAŁYWANIA CYNKOWNI

Abstract: The work aimed at determining the susceptibility to zinc accumulation of soils exposed to potential influence of zinc-works. Estimation of soil zinc binding ability was conducted by a modified method suggested by H.P. Blume and G. Brummer, according to which soils are divided into 5 classes differing with heavy metal accumulation ability depending on their physicochemical properties. The most important parameter of this division is soil pH, whereas the content of organic matter and < 0.02 mm particles fraction content in soil play an auxiliary role. Conducted assessment of zinc binding ability in soils revealed that in the area of potential influence of zinc-works, soils with low zinc accumulation ability have the biggest share. Among all analysed soils, 68 % of samples collected from the 0–10 cm layer and 58 % from the 40–50 cm layer reveal low or medium zinc binding abilities. Such high percentage of soils with these disadvantageous properties is mainly due to the fact that in these areas there is the highest number of acid soils with granular size distribution of loose sands. In case when the zinc-works starts operation, there is a serious potential of introducing excessive zinc amounts to food chain.

Keywords: soil, zinc, accumulation of zinc, pH, grain size distribution

The natural environment is constantly exposed to the effect of industrial emission, which to a considerable degree contributes to pollution of soil and other elements of the environment. Zinc is a component of many compounds emitted to the environment. Elevated zinc concentration in the environment is often connected with motorization, however industry also has its share in zinc emission [1]. Zinc compounds, such as: $ZnCl_2$, ZnO, zinc dust and ash are the main components of pollution created by zinc-works. Excessive industrial emission of zinc may contribute to a serious soil pollution with this metal. In some areas zinc pollution is considerable, which results among others in this metal accumulation in the close to the surface arable soil levels.

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The highest content of zinc occur in the areas where its ores are excavated and processed [1]. Zinc is one of more mobile metals in soil and its bioavailability is high due to very good solubility of its compounds. Higher plants take up zinc proportionately to its concentration in soil, therefore soil pollution with this metal may pose a hazard of its increased amount in food chain [2–4]. Apart from anthropogenic factor, zinc concentration in soil is also affected by a number its properties like: the kind of parent rock, grain size composition, soil pH or organic matter content [5].

Many authors have demonstrated that increase in soil acidity has a decisive influence on zinc solubility and therefore on its accumulative abilities in soil [3, 6]. It has been shown that in soil with neutral pH or slightly alkaline reaction zinc undergoes chemisorption on metal oxides and aluminosilicates and largely occurs in the form of organic complexes, so-called stable, hardly bioavailable zinc forms [7]. In case of slightly acid and acid soils, zinc is hardly complexed by organic substance, becomes mobile and is present in the soil solution as free ions, so-called labile zinc forms [8]. Other authors reported that a high solubility of zinc falls on soil pH below 4.5, whereas its strong binding in soil occurs when pH exceeds the value of 7 [9, 10]. The research aimed at determining possible zinc accumulation in soils in the zone of potential zinc-works influence.

Materials and methods

Field research was conducted in July 2010 in Trzcianka district, the area of potential influence of newly constructed zinc-works where production did not start until the end of 2011. In compliance with the Environmental Decision [11], planned yearly volume of production conducted by means of zinc flame spraying will be between 25 000 and 40 000 Mg of steel, at the maximum productivity reaching 10 Mg $\cdot$ h^{-1}.Trzcianka district is situated in the north-eastern part of Wielkopolska region, on the border of Pojezierze Waleckie and Pradolina Notecka, in the czarnkowsko-trzcianecki county. It is the area of high natural and tourist values, of which 50 % is covered by forests, whereas its western and central parts are interspersed with numerous lakes. The eastern part of the district, about 10 km from the zinc-works is a part of the Natura 2000 area [11].

The sampling places were planned so as to make possible estimating the extent and range of the zinc-works under construction influence on the natural environment. Square net was chosen as the method of sample collection in the immediate vicinity of the investment. Soil samples for analyses were collected from two layers (0–10 and 40–50 cm) in 19 points (Fig. 1) distanced from the centre of the zinc-works area by a 0.5, 1 and 5 km to the north, east, south and west and from the points situated at the distance of 0.7 and 1.4 km in the indirect directions of the first degree (NE, SE, SW, and NW). The sample collection points were localised using Garmin GPSap62s satellite receiver.

Basic physicochemical properties were assessed in the collected soil material: grain size distribution (Casagrande's method in Proszynski's modification), pH (by potentiometer in 1 mol $\cdot$ dm^{-3} KCl suspension) and organic matter content (by Tiurin's method).

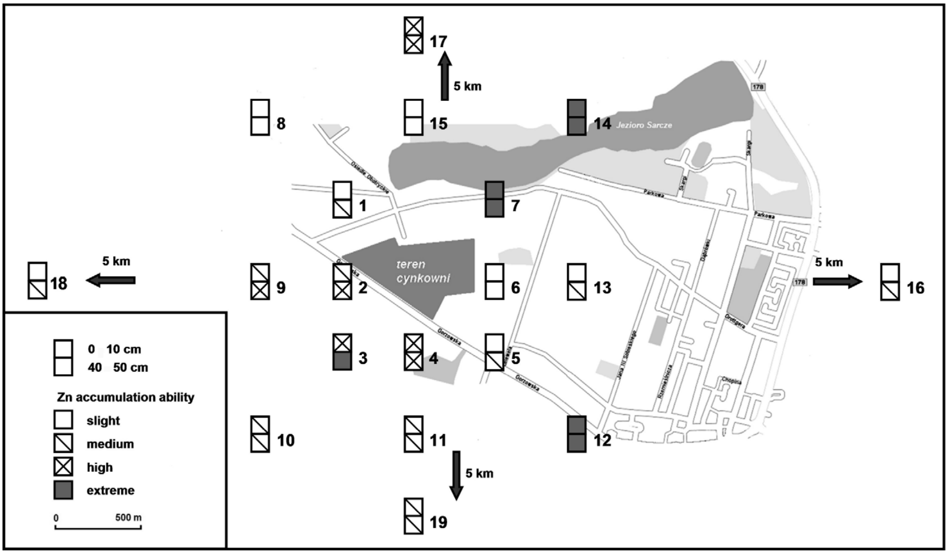

Fig. 1. Distribution of sampling sites and the ability to accumulate zinc in the topsoil (0–10 cm) and subsoil (40–50 cm)

In order to determine total zinc content, the soil material was dissolved in the mixtures of HNO_3 and $HClO_3$ acids (3 : 2). Zinc content in the obtained filtrates was assessed using ICP-OES method on Optima 2300 DV apparatus (Perkin Elmer).

Soil capability for zinc binding was assessed using the technique suggested by Blume and Brummer [12] and Gambus et al [7]. The assessment considers three basic physicochemical soil properties: pH (KCl), organic matter content and granular size composition. These parameters allow to classify a soil to a scale from 0 to 5. Class 0 denotes lack of zinc binding possibility, whereas class 5 comprises soils with a very high capability of this metal accumulation. The way of assigning a soil to a determined class was presented in Table 1.

Table 1

Influence of soil properties on its zinc accumulation ability (Zn acc)

pH_{KCl}	Zn acc	Content of organic matter [%]	Zn acc	Content of fraction < 0.0 [%]	Zn acc
2.5 3	0 1	0–2	0	< 20	0
3.5 4	1.5 2	2–8	0	20–35	0.5
4.5 5	2.5 3	8–15	0.5	35–50	0.5
5.5 > 6	4 5	> 15	0.5	> 50	1

The determining parameter is soil pH, while an adequate content of organic matter and floatable particles may correct the class number by 0.5 or one unit.

The results were verified statistically using Statistica 10 packet.

Results and discussion

Selected properties of analysed soils were presented in Table 2. In the vicinity of the zinc-works, soils with acid pH prevailed in the in the 0–10 cm layer (47 %), soils with slightly acid pH constituted (32 %). Neutral or very acid soils constituted 11 %. In the 40–50 cm layer, slightly acid soils prevailed (42 %), acid ones made up (32 %) and neutral ones (16 %). Very acid soil made up only 5 %. Analysis of grain size composition revealed that 79 % of soils from the 0–10 cm layer and 74 % from the 40–50 cm layer were very light soils, whereas the other 11 % and 16 % were light soils (Table 2).

Table 2

Selected physico-chemical properties of soils from the area of galvanizing plant

No. of sample	pH_{KCl}		Fraction < 0.02 [%]		Organic matter [g · kg^{-1} d.m.]		Zn [mg · kg^{-1} d.m.]	
	0–10 cm	40–50 cm	0–10 cm	40–50 cm	0–10 cm	40–50 cm	0–10 cm	40–50 cm
1	4.82	5.40	8	6	10.5	12.5	36.1	20.4
2	5.45	5.80	9	7	34.6	38.5	25.1	111.6
3	5.86	6.05	11	4	19.2	28.3	50.8	163.4
4	5.85	5.96	10	4	12.2	16.4	25.1	19.0
5	4.69	5.29	6	11	12.2	11.1	46.1	84.3
6	4.06	4.22	7	6	6.9	16.2	19.3	47.4
7	6.89	6.95	15	13	28.7	5.5	29.7	96.8
8	4.23	4.98	7	5	5.3	4.5	20.2	19.7
9	5.16	5.54	5	5	34.8	33.2	27.8	36.3
10	5.23	5.30	7	4	33.5	32.0	50.6	39.4
11	5.25	5.45	5	3	15.4	15.9	43.6	32.0
12	6.54	6.98	15	10	6.0	5.6	248.1	228.0
13	4.96	5.08	12	16	14.5	15.6	27.6	209.7
14	6.42	6.65	8	10	20.5	18.9	25.0	22.8
15	4.29	4.39	5	5	25.7	24.5	17.6	14.6
16	4.45	4.66	8	13	33.0	28.9	55.2	31.0
17	5.94	6.00	6	4	42.2	27.8	40.7	60.6
18	4.97	5.23	9	15	9.7	8.7	39.0	27.8
19	5.21	5.23	3	7	14.5	13.2	17.7	20.5
Minimum	4.06	4.22	3	3	5.3	4.5	17.4	14.6
Maximum	6.89	4.98	15	16	42.2	33.2	248.1	228.0
Mean	5.28	5.53	8	8	19.7	17.5	44.6	57.5
Median	5.21	5.40	8	6	15.4	16.1	29.7	36.3
VC [%]	15	14	40	53	58	55	89	82

Organic matter content in the soil samples from both analysed layers was similarly diversified. Its average content in the top layers was higher than the content noted in the subsoil, respectively 19.7 and 17.5 $g \cdot kg^{-1}$ d.m. (Table 2).

Among the analysed physicochemical parameters, zinc content proved the most diversified. The research revealed highly varied concentrations of this metal in soil collected in the vicinity of zinc-works V = 89 % (0–10cm) and 82 % (40–50 cm). Mean content of zinc in the topsoil of the studied soils was 44.6 mg (median 29.7 mg) and fluctuated from 17.4 to 248.1 $mg \cdot kg^{-1}$ d.m. In the deeper layer, *ie* 40–50 cm zinc content ranged from 14.6 to 228 mg, at average content 57.5 $mg \cdot kg^{-1}$ d.m. (median 36.3 mg). Such big difference between arithmetic means and values of medians results from the fact that among the studied samples were single soils with definitely higher content of zinc than the others. Large quantities of this element were assessed particularly in the soil from point 12 (Fig. 1), situated in the strongly urbanized area in the immediate vicinity of industrial plants and communication routes (Table 2). Similarly, a relatively high concentrations of zinc in the subsoil samples from points 3 and 13 is probably due to human activities. It is also worth mentioning that in almost a half of studied soils, higher zinc content were registered in the 40–50 cm layer in relation to its content in the topsoil, which might have been caused by the grain size composition of the analysed soils, low pH and considerable mobility of the metal.

Classification of zinc accumulation ability in soils in the zinc-works neighbourhood was presented in Fig. 1 and Table 3.The assessment of zinc binding in soil in the 0–10 cm level indicates a prevalence in the area of soils with low zinc binding ability (42 %). Soil with medium zinc binding ability constituted 26 %, whereas those with high and very high ability, respectively 16 % each. The main reason of this state is prevalence of light and very light soils with acid pH in this area. In the 40–50 cm layer, soil with medium zinc binding ability predominated (43 %), the next were soils with high and very high ability (21 %) and those with low ability (16 %) (Table 3).

Table 3

Classification of zinc accumulation ability in soils from the area of galvanizing plant

Zn accumulation ability	Soil class	Soils			
		0–10 cm		40–50 cm	
		number	% share	number	% share
Slight	2	8	42	3	16
Medium	3	5	26	8	42
High	4	3	16	4	21
Extreme	5	3	16	4	21

Spatial distribution of individual classes of zinc binding ability in the studied soils indicates a certain dependence on the metal distribution in the topsoil. In the immediate vicinity of the zinc-works (points 1–7), in the 0–10 cm level soils with low zinc binding ability prevail (43 % of samples), which at the same time are soils with low total content of this metal (Fig. 1, Table 2). In the 40–50cm layer in the same points soils with very high, high and medium zinc accumulation ability constituted, respectively 29 % each and those with low ability 14 %. At the same time, soil in this layer revealed a higher zinc content than soil in the 0–10 cm layer (Fig. 1, Table 2).

Zinc is an element commonly occurring in the earth's crust, its mean content in soils fluctuates from 30 to 125 mg $\cdot$ kg^{-1} [2]. High concentration of zinc in soil negatively affects its properties. Zinc content over 100 mg $\cdot$ kg^{-1} d.m. of soil hinders nitrification processes, whereas concentrations over 1000 $\cdot$ kg^{-1} d.m. of soil negatively affect a majority of microbiological processes [1]. Research conducted by other authors [5] revealed that zinc toxic effect on plants, depending on their species and soil properties, appears at the concentrations of between 100 and 500 mg $\cdot$ kg^{-1}. Among the analysed 19 soils only one sample from the 0–10 cm layer and 4 from the 40–50 cm layer contained more than 100 mg Zn $\cdot$ kg^{-1} d.m. According to the assessment suggested by the researchers from IUNG-PIB in Puławy, which distinguished a 6-degree soil classification with respect to heavy metal content, considering the soil reaction and grain size distribution, 3 % of the analysed soils revealed natural (0 degree) Zn content, 37 % elevated concentrations (degree I), 34 % a weak pollution (degree II), 16 % medium pollution (degree III) and 11 % showed strong pollution (degree IV) [13]. On the other hand, according to the Decree of the Minister of the Natural Environment of 9 September 2002 on the soil standards and earth quality standards [14] the analysed soils were not polluted with zinc.

Conclusions

1. Assessment of zinc binding ability in soils in the 0–10 cm layer in the area of potential influence of zinc-works indicates a prevalence in the region of soils with low zinc binding ability with simultaneous low total content of this metal.

2. Due to prevalence in the area of potential zinc-works influence of acid and very acid soils characterised with low abilities to mobilise heavy metals, once the production starts in the zinc-works, there is a high probability of excessive amounts of zinc penetrating the food chain.

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OCENA MOŻLIWOŚCI AKUMULACJI CYNKU W GLEBACH W STREFIE POTENCJALNEGO ODDZIAŁYWANIA CYNKOWNI

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Abstrakt: Celem pracy było określenie podatności na akumulację cynku gleb narażonych na potencjalne oddziaływanie cynkowni. Oszacowanie zdolności gleb do wiązania cynku przeprowadzono zmodyfikowaną metodą zaproponowaną przez Blume i Brümmera, zgodnie z którą gleby dzieli się na 5 klas różniących się zdolnością akumulowania metali ciężkich w zależności od ich właściwości fizyczno-chemicznych. Najważniejszym parametrem tego podziału jest odczyn gleby, zaś pomocniczą rolę odgrywają zawartość materii organicznej i frakcji o średnicy cząstek < 0,02 mm w glebie. Przeprowadzona ocena zdolności wiązania cynku w glebach wykazała, że na terenie potencjalnego oddziaływania cynkowni największy udział mają gleb o małej zdolności akumulowania cynku. Spośród wszystkich przeanalizowanych gleb aż 68 % próbek pobranych z warstwy 0–10 cm i 58 % z poziomu 40–50 cm charakteryzuje się małymi lub średnimi możliwościami wiązania cynku. Tak duży odsetek gleb właśnie o tak niekorzystnych właściwościach jest spowodowany głównie tym, że na badanym obszarze najwięcej jest gleb kwaśnych o składzie granulometrycznym piasków luźnych. W przypadku uruchomienia produkcji cynkowni istnieje duże prawdopodobieństwo wprowadzenia nadmiernych ilości cynku do łańcucha troficznego.

Słowa kluczowe: gleba, cynk, akumulacja cynku, pH, skład granulometryczny

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EFFECTS OF ULTRASOUND DISINTEGRATION OF MAIZE SILAGE ON THE EFFICIENCY OF METHANE FERMENTATION

WPŁYW ULTRADŹWIĘKOWEJ DEZINTEGRACJI KISZONKI KUKURYDZY NA EFEKTYWNOŚĆ FERMENTACJI METANOWEJ

Abstract: This article analyses the impact of using ultrasound in the pretreatment of maize shoots on the process of anaerobic digestion. The analysis was conducted to demonstrate the impact of ultrasound to improve the methane fermentation of maize silage by the anaerobic degradation of structural lignocellulose. Tests were performed on a test bench consisting of a two-stage reactor system, the first stage of which served as a control, while the substrate used in the second stage was exposed to ultrasound. In the present two-stage methane fermentation system, a significant decrease in COD values from baseline values was observed (84 %), while in the case of the control system not treated with ultrasound, a pollutant removal efficiency of 77 % was observed. In the test system, an increase of 30 % in the amount of biogas produced was observed compared with the control system.

Keywords: anaerobic digestion, biogas, ultrasound, lignocellulosic biomass

The development of the renewable energy industry is of crucial importance for implementation of the basic aims of the energy policy in Poland. Energy production from renewable sources ensures positive ecological effects and contributes to the growth of under-developed regions. Currently, renewable energy resources make up about 14 % of globally-consumed energy, of which up to 10 % is derived from biomass. This source is considered to be an alternative to fossil fuels [1]. As regards biomass transformation, a commonly-applied method is methane fermentation, which is a cost-

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-effective and environmentally-friendly method of energy generation [2]. In order to increase the efficiency of the fermentation process, it is necessary to perform preliminary treatment of substrates. Obtaining the highest possible decomposition of lignin and cellulose structures during the pretreatment process is very important for achieving the best results. Numerous studies have been carried out to improve the fermentation process, with the focus on examining the effects of various factors leading to obtaining methane-rich biogas [3]. The research described in this paper concerns the effects of pretreatment of maize shoots with ultrasound on the process of methane fermentation. The performed analyses aimed at demonstrating the effects of ultrasound on improvement of the methane fermentation of maize shoots through abiotic degradation of lignin and cellulose structures.

Ultrasound waves are acoustic waves in the frequency range from 16 kHz to 100 MHz. Ultrasound, due to its specific interaction with matter, is widely applied in medicine, technology, industry and cosmetology. In nature, it is used by animals for echolocation purposes and has both a passive and active impact on the environment in which it propagates. The most important passive applications include ultrasound defectoscopy, hydrolocation and (extremely important in modern medicine) ultrasound diagnostics. Passive application consists of generating and detecting ultrasound waves with an intensity which does not destroy the structure of the given medium. Each change to the status or the properties of the medium brings about a change in the conditions for acoustic wave propagation. A sufficiently high intensity of ultrasound waves can trigger cavitation capable of disintegrating microorganisms, viruses, bacteria as well as plant and animal cells [4, 5].

Ultrasound is increasingly often applied in the disintegration of plant structures to accelerate their hydrolysis [6]. As a result of ultrasound activity, intracellular substances are degraded and released to water. Ultrasound waves cause changes in the chemical structure and efficiency of biological membranes, which leads to disintegration of intracellular substances. It also has a favourable effect on releasing sugars from lignin and cellulose structures, making those sugars more easily accessible to microorganisms performing the fermentation process [4].

Materials and methods

Maize, previously ground and dried at 80 ^{o}C, was used as a substrate in the experiment. The substrate prepared in this manner was hydrated to 95 % and placed in a 15 dm^3 tank. The content of the tank was continuously mixed with the use of an electric mixer. From the tank, the hydrated substrate was pressed with the use of peristaltic pumps into two anaerobic reactor systems. In the reactors, the introduced substrate was heated to 37 ^{o}C by means of electric heaters.

The test stand (Fig. 1) was composed of two two-stage reactor systems: the first system was used for control purposes, while the substrate used in the other system was subjected to ultrasound. The device emitting ultrasound waves was placed on a glass flow cylinder, into which the substrate was inserted before being sent to the reactor systems. The inflow of sewage to the reaction chambers was periodic. During a 2 h

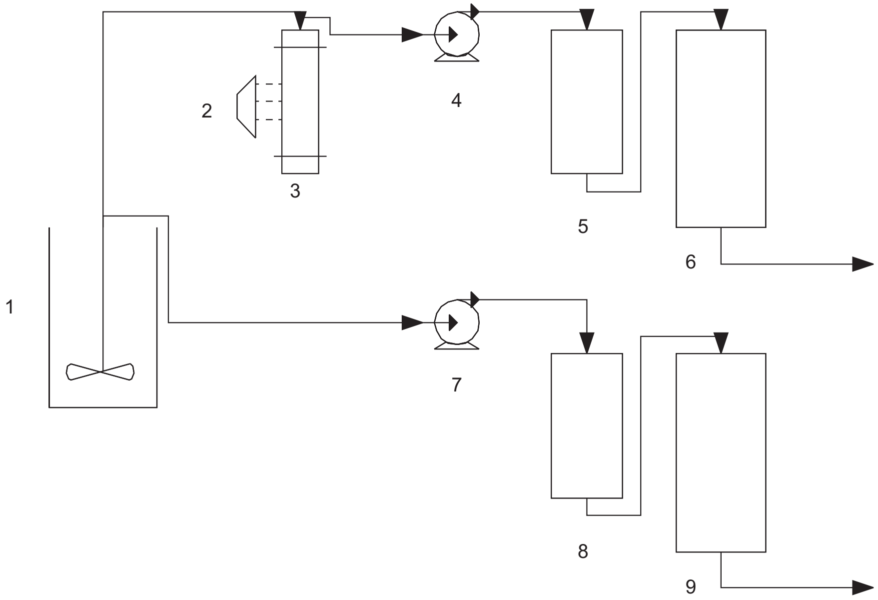

Fig. 1. Test stand: 1 – Substrate preparation chamber; 2 – Ultrasound emitter; 3 – Flow cylinder; 4 – Pump 1; 5 – Control reactor 1; 6 – Control reactor 2; 7 – Pump; 8 – Test reactor 1; 9 – Test reactor 2

cycle of sewage supply, the pumps operated for 8 minutes at a specified efficiency level. The reactor load averaged 1600 g/m^3d.

The analyses were carried out after operating the reactors for 24h. The scope of analyses included examination of COD values, pH analysis and a quality and quantity examination of the biogas produced.

Results

The level of *chemical oxygen demand* (COD) in the test systems is presented in Fig. 2. The control system was characterized by a 21 % lower value of COD in untreated sewage than the test system, in which sewage was subjected to ultrasound. In the test system, reduction of COD in the first reactor was 54 % in comparison with sewage subjected to ultrasound, while in the control system it was only reduced by 35 % in comparison with untreated sewage. The value of COD at the end of the systems was 456 mgO_2/dm^3 for the control system, which was 77 % lower than the initial value, while for the test system it amounted to 400 mgO_2/dm^3 and was 84 % lower than the initial value.

The pH in case of both systems in the reactors fluctuated around 6 and in reactor 2 – around 7.

The quality analysis of the biogas (Fig. 3) revealed that the quality of biogas produced was better in the test system, for both sequences, in both the first and second reactor.

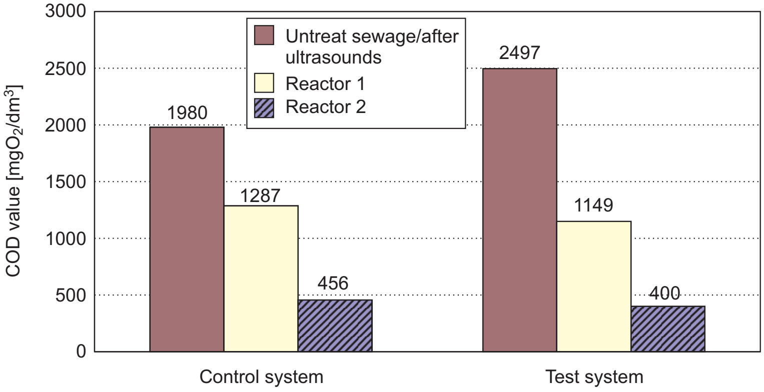

Fig. 2. Level of chemical oxygen demand in test systems

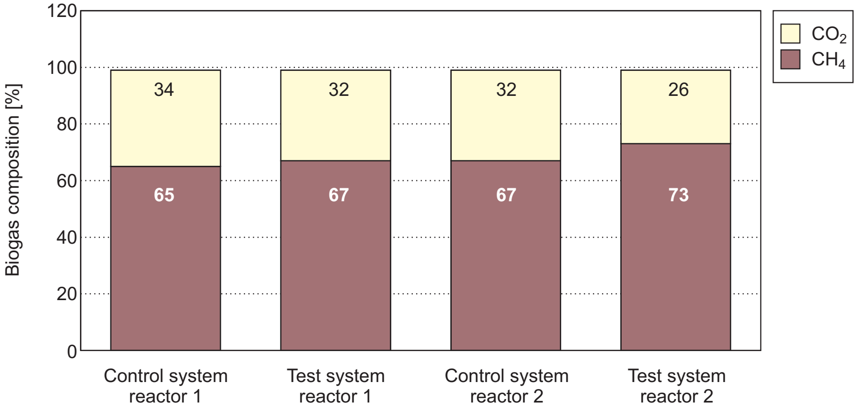

Fig. 3. Quality composition of the biogas produced in the control system and the test system

The quantity analysis of the biogas demonstrated that an average daily increase of the gas produced in the test system in reactor 1 was 1.7 dm^3, while this value for in the same reactor in the control system amounted to 1.2 dm^3, *ie* it was by 30 % lower. In reactor 2 in the system with ultrasound, the average daily increase was 1.6 dm^3, and in the control reactor it was 1.1 dm^3, which was lower by 31 %.

Results and discussion

The application of ultrasound is a very efficient pretreatment method commonly applied to increase sludge susceptibility to biodegradation. This method has been successfully used to solve problems related to the sludge management of sewage treatment plants. Alastair et al reported that as a result of ultrasound, the production of biogas grows by 34 % compared with sludge not treated with USG [7]. Similar conclusions were drawn by Benandallah et al who, observed that ultrasound was able to remove harmful benzopyrene and naphthalene from sludge, in addition to an increase in daily production of biogas by 23 % [8]. These phenomena were observed while carrying out fermentation under both thermophilic and mesophilic conditions. Bougrier et al examined the effect of ozoning, ultrasound and thermal treatment on increases in the efficiency of anaerobic sludge fermentation [9]. The three kinds of treatment mentioned above were carried out under the same conditions, on the same sludge samples. Ultrasound proved the most efficient as regards susceptibility to anaerobic decomposition. Taking into account methane production, the results obtained with ultrasound were similar to the thermal treatment; in both cases methane production grew by about 34 %. Erden et al examined the application of low frequency ultrasound for pretreatment of sewage originating from meat production. The application of this type of treatment improved methane production by 24 % [10]. As follows from the data quoted in the literature and from results of own research, the application of ultrasound is justified in the case of pretreatment of sludge, sewage and biomass before the process of biogas production.

Conclusions

The analysis of the results demonstrated that ultrasound had a favourable effect on quality improvement and on an increase in the amount of biogas produced during fermentation of maize shoots.

A significant drop in the COD values (84 %) was observed in the analysed two-staged system of methane fermentation. In the case of the control system not subjected to ultrasound, the recorded efficiency of impurity removal was 77 %. The test system revealed an increase in the amount of the produced biogas (by 30 %) in comparison with the control system. The composition of the gas obtained for both sequences was very similar.

Acknowledgements

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WPŁYW ULTRADŹWIĘKOWEJ DEZINTEGRACJI KISZONKI KUKURYDZY NA EFEKTYWNOŚĆ FERMENTACJI METANOWEJ

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Abstrakt: Badania opisane w artykule dotyczą wpływu wstępnej obróbki kiszonki kukurydzy za pomocą ultradźwięków na proces fementacji metanowej. Prowadzone analizy miały na celu wykazanie wpływu ultradźwięków na poprawę fermentacji metanowej pędów kukurydzy poprzez abiotyczny rozkład struktur lignino-celulozowych. W analizowanym dwustopniowym układzie fermentacji metanowej zaobserwowano znaczny spadek wartości ChZT w stosunku do wartości wyjściowej, było to 84 %, w przypadku układu kontrolnego nie poddanego działaniu ultradźwięków zanotowano sprawność usuwania zanieczyszczeń na poziomie 77 %. W układzie badawczym zaobserwowano wzrost ilości produkowanego biogazu o 30 % w porównaniu z układem kontrolnym.

Słowa kluczowe: fermentacja metanowa, biogaz, ultradźwięki, biomasa lignocelulozowa

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THE ACTIVITY OF SELECTED SOIL ENZYMES, AND SOIL CONTAMINATION WITH ZINC, CADMIUM AND LEAD IN THE VICINITY OF THE ZINC SMELTER "MIASTECZKO SLASKIE"

AKTYWNOŚĆ WYBRANYCH ENZYMÓW GLEBOWYCH ORAZ ZANIECZYSZCZENIE GLEBY CYNKIEM, OŁOWIEM I KADMEM W SĄSIEDZTWIE HUTY CYNKU „MIASTECZKO ŚLĄSKIE"

Abstract: Heavy metals are a serious source of soil pollution, especially in the vicinity of metal smelters. This study examines the effect of selected heavy metals on the activity of soil enzymes (acid phosphatase, dehydrogenase, β-glucosidase, urease and protease) in topsoil (0–30 cm) in the vicinity of the zinc smelter "Miasteczko Slaskie". Soil enzyme activity in the polluted site was compared with a non-polluted site in the outskirts of the Pazurek nature reserve (near Olkusz). Soil samples were collected in coniferous communities. The activity of soil enzymes were compared at distances of 0.5 km, 1 km and 1.5 km from the emitter. In the vicinity of the emitter (all distances) Cd, Pb and Zn levels in topsoil exceeded acceptable limits. Also, Pb content at a non-polluted site (Pazurek nature reserve) was higher than permissible levels. Zn (HNO_3 extracted) were the highest in the topsoil samples collected at a distance of 1.5 km from the Miasteczko Slaskie plant, Cd (HNO_3 and $CaCl_2$ extracted) and Pb ($CaCl_2$ extracted) contents were highest at the distance 1 km from the emitter. However, the pollution index in the superficial soil layer (0–10 cm) was similar at all three distances from the emmiter. The Zn, Cd and Pb bioavailable concentrations ($CaCl_2$ extracted) ranged: 15–220, 0.1–7.2, 2.8–55.7 $mg \cdot kg^{-1}$ respectively. The greatest decreases were found for acid phosphatase, dehydrogenase and protease activity at the distance of 0.5 km from the emitter. Results show that soil enzymatic activity should accompany basic chemical analysis to track disorders and adverse effects in polluted soil.

Keywords: soil enzyme activity, heavy metals

Heavy metal pollution is a major environmental concern. In recent decades there has been an increasing interest in the long term effect of heavy metals at high concentration due to their persistence in soil for tens or even thousands of years [1, 2]. The presence of heavy metals in soil may influence biochemical processes by affecting both microbial

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proliferation and enzyme activity. Comparative studies have reported reductions in microbial biomass or soil enzyme activity in acidic forest soils exposed to long-term atmospheric deposition of metals from smelters [1, 3]. Microbiologically mediated processes, catalyzed by enzymes, are essential for the functioning of soil, providing the basis of carbon, nitrogen, phosphorous and sulfur cycles in soil. Therefore soil enzymes can be used as responsive indicators of the impact of metals on soil biochemical properties involved in carbon and nutrient cycles [4, 5]. In this study, we investigated the effect of soil pollution by Zn, Pb and Cd on the activities of acid phosphatase, dehydrogenase, β-glucosidase, urease and protease in topsoil of coniferous sites along a deposition gradient in the vicinity of the zinc plant "Miasteczko Slaskie". Soil enzyme activity in the polluted site was compared with a non-polluted site in the outskirts of the Pazurek nature reserve (near Olkusz). To this end, we determined and compared soil levels of Zn, Pb and C (acid extracted and potentially bioavailable).

Material and methods

Five topsoil samples from soil layers 0–10 cm, 10–20 cm and 20–30 cm were collected from the vicinity of the zinc smelter "Miasteczko Slaskie" (at distances of 0.5 km (M1), 1 km (M2) and 1.5 km (M3)). In June 2009 samples were collected from 5 random sites from an area of 50 m^2, each from a eastern direction. Soil was also collected from a coniferous forest ecosystem on the perimeter of the Pazurek nature reserve near Olkusz (P), selected as a potentially contamination-free control area. The soil enzyme activity was determined in soil samples at field moisture, sieved through a 2 mm sieve and stored at 4 ^{o}C before microbial analysis. The activity of alkaline and acid phosphatase was measured according to the method of Schinner et al [6]. The *p*-nitrophenol (NP) released by phosphomonoesterase activity was extracted and colored with sodium hydroxide and determined photometrically at $\lambda = 400$ nm. The phosphatase activity was expressed in μg *p*-nitrophenol (*p*-NP) g^{-1} d.m. h^{-1} (d.m. – dry matter). The urease activity estimation was based on the colorimetric determination of ammonium formation after enzymatic urea hydrolysis (10 % solution, λ – 630 nm). Urease activity was expressed as μgN · g^{-1} d.m. [6]. Protease activity was determined using casein as substrate. Aromatic amino acids react with Folin-Ciocalteu's phenol reagent in alkaline solution to form a blue complex which was determined colorimetrically at $\lambda = 700$ nm. Protease activity was expressed in μg tyrosine g^{-1} d.m. h^{-1}. Saligenin released from salicin (β-glucosido-saligenin) was determined colorimetrically after coloring with 2,6-dibromchinon-4-chlorimide, at $\lambda = 578$ nm in β-glucosidase activity estimation. β-glucosidase activity was expressed as μg saligenin g^{-1} d.m. h^{-1}. Triphenyltetrazolium chloride was the substrate which was used for the dehydrogenase activity determination. Triphenyl formazan (TPF) was extracted with acetone and measured photometrically at $\lambda = 546$ nm. The dehydrogenase activity was expressed in μg triphenyl formazan (TPF) g^{-1} d.m. h^{-1} Schinner et al [6]. The metal concentrations in the soil samples were estimated according to the method of Bouwman et al [7] and Ostrowska et al [8]. The air-dried soil samples were sieved through a 1 mm sieve and used for metal extraction with 0.01 M $CaCl_2$ (potentially bioavailable elements) or with 10 % HNO_3 (acid extracted elements). During $CaCl_2$ extraction, 5 g of soil with 50 cm^3 of 0.01 M $CaCl_2$ solution was shaken for 5 h. An HNO_3-extractable fraction was obtained by shaking a sample (10 g) with 100 cm^3 of 10 % HNO_3 for 1 h. The contents of metals were measured in the filtered extracts. The *soil pollution index* (SPI) was calculated for each locality according to the equation given below [9] and was based on limit values as reported in [16]. The limit values (permissible concentrations) of heavy metals in soils were: Zn – 300 $mg \cdot kg^{-1}$, Pb – 100 $mg \cdot kg^{-1}$, Cd – 4 $mg \cdot kg^{-1}$.

$$SPI = \frac{1}{n} \cdot \sum_{i=1}^{n} \cdot 100 \cdot \frac{VS_i}{LS}$$

were: n – number of elements,
VS – content of an element in the soil [$mg \cdot kg^{-1}$],
LS – limit value for an element in the soil [$mg \cdot kg^{-1}$].

The results are presented as means of five replicates of each estimation, together with standard deviation (SD) of the means. The data was processed using Statistica software to compute significant statistical differences between samples ($p < 0.05$) according to Tukey's multiple range test and to compute Pearson's correlation coefficients.

Results and discussion

In most cases heavy metal concentrations in the fractions of soil extracted with HNO_3 and in the fractions of soil extracted with $CaCl_2$ decreased with soil depth. Generally the highest investigated metal content were found in the superficial soil layer (0–10 cm). The highest Zn contents (acid extracted) were found 1.5 km from the emitter – the zinc smelter "Miasteczko Slaskie". The highest Pb ($CaCl_2$ extracted) and Cd contents were found at a distance of 1 km from the emitter. In acid extracted soil fractions heavy metal contents ranged for Zn 19.7–1062.3, for Cd 0.8–27.3 and for Pb 37.1–2518.5 $mg \cdot kg^{-1}$, respectively. Several to almost two hundred times lower concentrations of the metals examined were measured in the potentially bioavailable fractions ($CaCl_2$ extracted) (Table 1). However the pollution index (estimated for acid and $CaCl_2$ extracted metal concentrations) in the superficial soil layer (0–10 cm) was at a comparable level at all distances from the emitter (except M2, HNO_3). HNO_3-extraced heavy metals in the vicinity of the emitter (at all distances 0–10 cm) were higher than acceptable limits for soil according to the Environmental Regulation (2002) (Zn 300 $mg \cdot kg^{-1}$, Pb 100 $mg \cdot kg^{-1}$ and Cd 4 $mg \cdot kg^{-1}$). In our study Pb content in the samples collected in the similar coniferous forest ecosystem on the perimeter of the Pazurek nature reserve in the soil layer 0–20 cm was above the permissible concentration [10]. In our previous study in the vicinity of the former "Szopienice" plant in Katowice, we found higher Zn and Cd concentration and lower Pb concentration [4]. In the superficial soil layer in the vicinity of the Szopienice plant and at a calamine site in Dabrowa Gornicza and in zinc wastes heap located in Katowice, the bioavailability of the metals was low and at comparable levels to this present study. Olszowska et al found similar levels of heavy metals in the soil of the pine coniferous forest of age class III in threat

Table 1

Mean heavy metal content in the surface soil layer in the vicinity of zinc smelter Miasteczko Slaskie and in Pazurek. Values with the same letter are statistically the same for $p < 0.05$

Sampling sites	M1 (0–10)	M1 (10–20)	M1 (20–30)	M2 (0–10)	M2 (10–20)	M2 (20–30)	M3 (0–10)	M3 (10–20)	M3 (20–30)	P (0–10)	P (10–20)	P (20–30)
Zn (HNO_3)	419.3 ± 26.9 j	218.6 ± 6.7 d	151.0 ± 1.3 c	919.9 ± 60.4 i	765.6 ± 4.1 h	233.2 ± 11.1 d	1062.3 ± 66.7 g	520.3 ± 51.4 f	188.4 ± 6.4 e	127.9 ± 16.4 c	54.8 ± 2.6 b	19.7 ± 0.2 a
Zn ($CaCl_2$)	198.7 ± 4.3 g	89.5 ± 1.6 d	98.7 ± 2.8 e	97.9 ± 2.5 e	220.1 ± 6.2 f	101.7 ± 1.2 e	140.4 ± 24.9f	124.9 ± 9.6 f	85.1 ± 2.2 d	46.42 ± 1.34 c	21.8 ± 0.3 b	15.1 ± 1.7 a
Cd(HNO_3)	7.9± 0.3d	2.6 ± 0.8 ab	4.9 ± 0.3 c	27.3 ± 0.6 g	16.4 ± 1.3 f	8.8 ± 0.4 d	19.5 ± 0.4 h	11.41 ± 0.19 e	3.9 ± 0.1bc	1.8 ± 0.1a	3.7 ± 0.4 bc	0.8 ± 0.01a
Cd ($CaCl_2$)	4.8 ± 0.7 c	2.3 ± 0.3 b	3.4 ± 0.1 c	7.2 ± 4.1 d	4.7 ± 0.1 c	3.2 ± 0.1 c	4.4 ± 0.5 c	2.1 ± 0.1 b	1.1 ± 0.1 b	1.6 ± 0.1 b	0.34 ± 0.2 a	0.13 ± 0.01 a
Pb (HNO_3)	2055.5 ± 151.5 i	355.7 ± 1.2 d	2518.5 ± 134.5 h	569.8 ± 7.1 g	431.9 ± 6.5 f	291.1 ± 22.4 c	1809.1 ± 43.2 j	388.1 ± 0.8 e	247.7 ± 12.5bc	229.1 ± 3.7 b	195.5 ± 13.1 b	37.1 ± 0.05a
Pb ($CaCl_2$)	16.5 ± 3.1 b	16.8 ± 0.6 b	13.2 ± 2.3 b	55.7 ± 19.2 a	41.8 ± 0.5 a	7.4 ± 0.1 c	16.2 ± 1.7 b	3.6 ± 0.1 c	6.5 ± 0.3 c	5.9 ± 1.1c	2.8 ± 0.2 c	4.0 ± 0.4 c
Pollution index (HNO_3)	797.9 ± 50.9 e	164.6 ± 6.2 f	897.8 ± 47.2 e	519.4 ± 4.0 j	365.3 ± 9.5 h	197.0 ± 12.4 g	883.2 ± 25.3 e	282.2 ± 7.5 d	136.5 ± 5.3c	105.8 ± 0.5 b	102.0 ± 7.2 b	21.2 ± 0.04 a
Pollution index ($CaCl_2$)	67.8 ± 7.1 e	35.0 ± 2.2 c	43.7 ± 0.3 d	89.4 ± 40.4 ef	77.3 ± 1.6 f	40.4 ± 0.6 d	57.5 ± 7.3 e	32.0 ± 1.6 c	20.5 ± 0.8 b	20.1 ± 0.5 b	6.2 ± 1.6 a	4.1 ± 0.04 a

Table 2

Mean pH value. organic matter content in the surface soil layer the vicinity of zinc smelter Miasteczko Slaskie and in Pazurek. Values with the same letter are statistically the same for $p < 0.05$

Sampling sites	M1 (0–10)	M1 (10–20)	M1 (20–30)	M2 (0–10)	M2 (10–20)	M2 (20–30)	M3 (0–10)	M3 (10–20)	M3 (20–30)	P (0–10)	P (10–20)	P (20–30)
pH	5.63 ± 0.01a	5.66 ± 0.04 a	5.63 ± 0.02 a	5.25 ± 0.01 b	5.31 ± 0.01 c	5.425 ± 0.005 d	5.82 ± 0.01 e	5.985 ± 0.04 f	5.805 ± 0.01 g	5.21 ± 0.01 h	5.555 ± 0.01 i	5.42 ± 0.01j
Organic matter	3.3 ± 0.02 a	1.25 ± 0.09 b	1.32 ± 0.08 b	15.35 ± 0.03c	10.76 ± 0.02 d	3.34 ± 0.01 a	5.955 ± 0.06 e	4.39 ± 0.03 f	2.795 ± 0.01 g	7.055 ± 0.03 h	5.52 ± 0.18 i	1.17 ± 0.02 j

Table 3

Mean soil enzyme activity in the surface soil layer in the vicinity of zinc smelter Miasteczko Slaskie and in Pazurek. Values with the same letter are statistically the same for $p < 0.05$

Sampling sites	M1 (0–10)	M1 (10–20)	M1 (20–30)	M2 (0–10)	M2 (10–20)	M2 (20–30)	M3 (0–10)	M3 (10–20)	M3 (20–30)	P (0–10)	P (10–20)	P (20–30)
Acid phosphatase [μg *p*-NP $g^{-1} \cdot h^{-1}$]	3.0 ± 0.1 a	4.4 ± 0.4 a	20.7 ± 2.4 b	208.2 ± 24.9 c	42.5 ± 0.0 d	72.4 ± 2.0 e	31.0 ± 7.5 bg	25.9 ± 2.5 b	25.5 ± 2.4 b	109.3 ± 24.1 f	37.3 ± 0.8 g	8.5 ± 2.4 h
Dehydrogenase [μg TPF g^{-1} d.m. h^{-1}]	1.3 ± 0.0 a	2.5 ± 1.0 a	4.8 ± 1.0 bc	10.0 ± 1.1 e	3.7 ± 0.4 b	7.3 ± 0.9 d	12.6 ± 1.8 e	20.3 ± 1.8 f	4.1 ± 0.6 b	19.8 ± 1.5 f	12.6 ± 1.0 e	6.6 ± 0.2 cd
Urease [μgN g^{-1} d.m. h^{-1}]	80.1 ± 3.7c	39.2 ± 5.1a	82.2 ± 0.9 c	181.4 ± 15.7 e	137.1 ± 7.6 d	94.8 ± 8.1c	135.9 ± 12.3 d	71.6 ± 17.2 bc	42.7 ± 1.2 a	67.4 ± 0.9 b	44.0 ± 4.8 a	71.1 ± 10.9 bc
β-Glucosidase [μg saligenin g^{-1} d.m. h^{-1}]	5573.3 ± 293.3 g	1361.7 ± 179.1 ab	1741.4 ± 3.1 c	1023.0 ± 158.0 a	1447.8 ± 11.4 b	2005.4 ± 27.1 e	4266.5 ± 347.5 f	1717.0 ± 88.0 c	4060.6 ± 805.8 f	1913.0 ± 14.4 d	2292.9 ± 227.1 e	1176.0 ± 130.7 a
Protease [μg tyrosine g^{-1} d.m. h^{-1}]	2.4 ± 0.4 de	0.3 ± 0.1 a	0.7 ± 0.0b	4.3 ± 0.6 ef	3.1 ± 0.6e	1.9 ± 0.4 cd	2.1 ± 0.0 d	6.0 ± 0.6 g	1.4 ± 0.2 c	4.8 ± 0.6 f	5.4 ± 0.5 f g	0.5 ± 0.2 a

Table 4

Correlation coefficients between heavy metal content (acid extracted and bioavailable) in studied soil samples and enzyme activity. (Significant for $p < 0.05$)

	Zn (HNO_3)			Zn ($CaCl_2$)			Pb (HNO_3)			Pb ($CaCl_2$)			Cd (HNO_3)			Cd ($CaCl_2$)		
Soil layer	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30	0–10	10–20	20–30
Acid phosphatase			0.79	–0.64		0.62	–0.8			0.72			0.48	0.6	0.93			0.6
Dehydrogenase				–0.87			–0.73				–0.71	–0.48				–0.48	–0.51	
Urease	0.84	0.88			0.91			0.66		0.75	0.8		0.9	0.92	0.54	0.54	0.85	0.63
β-Glucosidase		–0.54	0.5	0.86	–0.66		0.92	–0.83		–0.48	–0.61						–0.74	
Protease	–0.41		0.84	–0.81		0.6	–0.92				–0.48				0.78			

zone III in the region of the activity of the smelter “Miasteczko Slaskie” (Zn – 437 mg · kg^{-1} d.m., Pb – 1002 mg · kg^{-1} d.m., Cd – 3.90 mg · kg^{-1} d.m.) [11].

The concentrations of Zn, Pb and Cd extracted with 0.1 M $NaNO_3$ (considered as bioavailable) in the study of the upper layer of the 100-year-old zinc-lead waste heap were also low and accounted for no more than 0.5 % of total concentrations in the heap material [12].

Determination of soil enzymatic activity can serve as a basis for evaluation of soil quality as enzymes are particularly susceptible to changes in the environment [13]. In this present study the greatest decreases were found for acid phosphatase, dehydrogenase and protease activity at a distance of 0.5 km from the zinc smelter “Miasteczko Slaskie”. The activity of β-glucosidase was lowest at a distance of 1 km from the emitter. Urease activity in soil collected at the distance of 0.5 km from the emitter was at a comparable level with the urease activity in the soil of non-polluted site. Many reports demonstrated significant inhibition of enzymatic activities by heavy metals. However, the effects of heavy metals on enzyme activity may vary considerably among the elements, enzymes and soils [1, 14]. The negative correlations between particular extracted heavy metal content and enzyme activity were found only in some cases (especially between Pb content (HNO_3 extraction), Zn content ($CaCl_2$ extraction) pollution index (HNO_3) and acid phosphatase, dehydrogenase and protease activity in the superficial layer (0–10 cm) (Tables 4, 5).

Table 5

Correlation coefficients between pollution index (established for acid extracted and bioavailable metals content) in studied soil samples and enzyme activity. (Significant for $p < 0.05$)

	Pollution index (HNO_3)			Pollution index ($CaCl_2$)		
Soil layer	0–10	10–20	20–30	0–10	10–20	20–30
Acid phosphatase	–0.54					0.6
Dehydrogenase	–0.7			–0.59	–0.5	
Urease		0.89		0.56	0.88	0.53
β-Glucosidase	0.71	–0.56			–0.71	
Protease	–0.87					

In many cases positive correlation coefficients between organic matter content and examined soil enzyme activity were stated (Table 6).

Some studies demonstrated a significant relationship between soil enzymes and other soil characteristics, but the relationship is largely dependent on the species of enzyme and environmental variables [15]. The content of organic substance or the soil pH can have a significant influence on the decrease of available forms of heavy metals and their biological inactivation [16, 17]. There are reports indicating that enzymes involved in the C cycle are less affected by heavy metals in contaminated soils than enzymes related to N, P, and S cycles and the expected reduction of activity is often not observed [1]. β-glucosidase activity was less affected in our study. However, intracellular activity of dehydrogenase involved in the C-cycle, was decreased in the emitter vicinity.

Extracellular enzymes adsorbed onto clay minerals can act for a long time in the soil because of increasing durability and denaturation and proteolysis resistance [18].

Table 6

Correlation coefficients between pH and organic matter content in studied soil samples and enzyme activity. (Significant for $p < 0.05$)

	pH			Organic matter content		
Soil layer	0–10	10–20	20–30	0–10	10–20	20–30
Acid phosphatase	–0.79	–0.49		0.94	0.89	0.83
Dehydrogenase	–0.47	0.75	–0.83			
Urease		–0.52	–0.72	0.78	0.88	
β-Glucosidase	0.83		0.8	–0.84		0.95
Protease	–0.93			0.58		0.92

Some authors proposed reduced enzyme activity (especially dehydrogenase, urease and phosphatase) as indicators of soil contamination with heavy metals [1]. This statement has been confirmed by our study in the case of acid phosphatase and dehydrogenase activity.

Conclusions

The dynamics and differences in the compared soils can be tracked by measuring enzymatic activity. The low bioavailability of the studied metals may be one of the reasons for their lower effect on the enzymatic activity. The greatest negative impact of examined metals was found for dehydrogenase and acid phosphatase activity. These enzymes activity were better in estimation of negative changes in soil. Hence, the study of enzymatic activity should be conducted in forest ecosystems and especially in those under anthropogenic pressure.

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AKTYWNOŚĆ WYBRANYCH ENZYMÓW GLEBOWYCH ORAZ ZANIECZYSZCZENIE GLEBY CYNKIEM, OŁOWIEM I KADMEM W SĄSIEDZTWIE HUTY CYNKU „MIASTECZKO ŚLĄSKIE”

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Abstrakt: Zanieczyszczenie gleby metalami ciężkim zwłaszcza w pobliżu hut metali to poważny problem. Oceniano wpływ metali ciężkich na aktywność enzymatyczną gleby. Celem badań była ocena aktywności enzymów glebowych: fosfatazy kwaśnej, dehydrogenaz, β-glukozydazy, ureazy i proteazy w wierzchniej warstwie gleby w najbliższym sąsiedztwie huty cynku Miasteczko Śląskie. Aktywność enzymatyczną gleby na stanowiskach zanieczyszczonych porównywano z aktywnością na stanowisku niezanieczyszczonym, próbki gleby pobierano również w pobliżu rezerwatu przyrody Pazurek koło Olkusza ze zbiorowisk borowych. Aktywność enzymatyczna w glebie najbliższego sąsiedztwa emitora była porównywana w odległości 0,5, 1, 1,5 km od emitora. Wykazane zawartości Cd, Pb i Zn przekraczały dopuszczalne normy przyjęte dla gleby. Zawartość Pb w próbkach gleby pobieranych w pobliżu rezerwatu Pazurek była wyższa niż dopuszczalne wartości dla gleby. Zawartość Zn (ekstrakcja HNO_3) była najwyższa w odległości 1,5 km od emitora (0–10 cm), z kolei zawartości Cd (ekstrakcja HNO_3 i $CaCl_2$) i Pb (ekstrakcja $CaCl_2$) były najwyższe 1 km od emitora. Wskaźnik zanieczyszczenia wykazany dla wierzchniej warstwy gleby (0–10 cm) był na porównywalnym poziomie w glebie w sąsiedztwie emitora. Koncentracje biodostępnych form metali (ekstrakcja $CaCl_2$) mieściły się w przedziałach odpowiednio: 15–220, 0,1–7,2, 2,8–55,7 mg · kg^{-1}. Najniższe aktywności fosfatazy, dehydrogenazy i proteazy wykazano w próbkach gleby pobieranej w odległości 0.5 km. Badania aktywności enzymatycznej gleby obok analiz chemicznych powinny być prowadzone w celu śledzenia zmian w glebach zanieczyszczonych.

Słowa kluczowe: aktywność enzymatyczna gleby, metale ciężkie

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