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CONTENTS

INDEXES

VARIA

SPIS TREŚCI

INDEXES

VARIA

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Anita SCHROETER-ZAKRZEWSKA[1]* and Tomasz KLEIBER[2]

APPLICATION OF SLOW-RELEASE FERTILIZERS IN GROWING MARGUERITE DAISY (*Argyranthemum frutescens*) Molimba® GROUP

ZASTOSOWANIE NAWOZÓW O SPOWOLNIONYM DZIAŁANIU W UPRAWIE SREBRZENIA KRZEWIASTEGO (*Argyranthemum frutescens*) Z GRUPY Molimba

Abstract: The aim of the conducted studies was to evaluate the effect of the application of slow-release fertilizers Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) and Osmocote Exact Standard 3–4 M (16 : 11 : 11) on growth and flowering of 3 cultivars from Molimba® group of marguerite daisy (*Argyranthemum frutescens)*. The height of plants, the number of inflorescence buds, the number and diameter of anthodia were determined, together with the state of nutrition of these plants with macro- and microelements. As a result of the conducted experiments it was found that depending on the variety both the type and the rate of the applied fertilizer had an effect on plant height. The application of a slow-release fertilizer with the predominating content of nitrogen, *ie* Osmocote Exact Standard (16 : 11 : 11), as well as a higher rate of Osmocote Exact Hi-K (11 : 11 : 18) resulted in a stronger growth of plants. An exception in this respect was found in cv. ‘Monroe Lemon Anemone’. In ‘Mini White Double’ and ‘Monroe Lemon Anemone’ flowering plants were produced as a result of higher rates of slow-release fertilizers. The type of fertilizer as well as its rate did not have a significant effect on the number of inflorescence buds or the diameter of anthodia. The cultivar had a significant modifying effect on the content of both macro- and microelements in plants. A significantly better nutrition of plants with phosphorus and iron was observed after the application of Osmocote Exact Standard 3–4 M (16 : 11 : 11) in comparison with Osmocote Exact Hi-K. Differences in the contents of the other macro- and microelements in plants recorded between the analyzed fertilizers were not significant. An increase in the rate of Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) had a significant effect on the state of nutrition of plants with potassium, manganese and zinc, while in case of Osmocote Exact Standard 3–4 M (16 : 11 : 11) it was for that of potassium and zinc. Taking into consideration the practical aspect, consisting in the simplification of cultivation methods under commercial production conditions as well as the quality of plants, and the ecological aspect (limitation of nutrient leaching outside the root zone of plants to groundwater, being hazardous to the natural environment), the tested slow-release fertilizers are suitable for the cultivation of marguerite daisy Molimba® group.

Keywords: slow release fertilizers, growth, plant nutrition, analysis of plants

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In recent years – due to their universal applications and very ornamental value--interest in the cultivation of bed plants has been increasing. Marguerite daisy is one such commercially available plant being in high demand. The rapid development of culture results in many new cultivars being offered every year, varying in their growth rates, colours, shapes and filling of anthodia. This provides an incentive for the undertaking of studies on optimization of their growing technology, focusing on plant nutrition, which is crucial for the production of good quality plants.

When growing many cultivars of marguerite daisy it is necessary to apply growth retardants in order to produce good quality plants [1]. In view of the increasing ecological restrictions it is attempted to reduce or eliminate the application of such substances. Growth of plants may be regulated, among other things, by appropriate plant nutrition, particularly with phosphorus [2].

The use of mixed slow-release fertilizers is an essential aspect in the simplification of cultivation methods [3] is of the opinion that balanced supply of nutrients during the whole growing period can be ensured by the use of slow-relase fertilizers. They are fertilizers, in which coatings exhibit properties determining the release of nutrients to the substrate. An example in this respect may be a resin coating of dicyclopentadiene copolymer with glyceride used in Osmocote Plus [4]. Typically the chemical composition of the coating is not disclosed as it is a business secret of the fertilizer manufacturer. The time and rate of nutrient release from slow-release fertilizers to a considerable degree is determined by temperature (the time of fertilizer activity is established for a temperature of 21 ^{o}C), while it does not depend on substrate reaction/moisture content or microbiological activity of the root zone [5]. The coating itself is degraded as a result of biodegradation. What is important, a slow-release fertilizer provides a significant simplification of the production cycle – once applied, it should supply nutrients to plants throughout their entire vegetation period. Thanks to the above, fluctuations in substrate salinity, disadvantageous for plants, may be avoided and leaching of nutrients outside the root zone of plants to groundwater, being hazardous for the natural environment, may be reduced. Leaching of nutrients to groundwater is the primary cause of its contamination in areas of intensive horticultural use [6]. Optimization of nutrition in other species, as well as suitability of slow-release fertilizers in growing ornamental plants have been discussed in earlier studies [7–16].

Due to a lack of data in literature concerning fertilizer recommendations the aim of the conducted investigations was to evaluate the suitability of slow-release fertilizers Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) and Osmocote Exact Standard 3–4 M (16 : 11 : 11), applied at 2 rates in container growing of different cultivars of marguerite daisy (*Argyranthemum frutescens*) from Molimba® group.

Material and methods

The studies was conducted at the Marcelin Experimental Station of the Poznan University of Life Sciences. Plants originating from Syngenta Seeds were planted to pots of 0.66 dm^3. Highmoor peat Klassman deacidified to pH 6.0 was used as a substrate. Slow-release fertilizers Osmocote Exact Hi-K 3–4 M (11 : 11 : 18 +

microelements) and Osmocote Exact Standard 3–4 M (16 : 11 : 11 + microelements) were added to the substrate. Each fertilizers was applied at two rates of 3 and 6 g · dm^{-3}. The experiments were conducted on three *Argyranthemum frutescens* Molimba® cultivars, *ie* ‘Mini White Double’ – with a compact habit, ‘Monroe Lemon Anemone’ – with a medium strong growth, and ‘Maggy Pastel Yellow’ – characterized by strong growth.

Biometric measurements were taken at the flowering phase of plants, concerning such traits as the height of plants, the number of inflorescence, the number of inflorescence buds and the diameter of inflorescence. Results of these measurements were statistically analyzed by the analysis of variance with the application of the Duncan test at the significance level $\alpha = 0.05$.

Chemical analyses

On the day the experiment was completed leaf samples were collected from plants for chemical analyses. Leaves were dried at 45–50 ^{o}C and then ground. In order to assay total forms of nitrogen, phosphorus, potassium, calcium, magnesium and sodium plant material was mineralized in concentrated sulfuric acid. Mineralization for assays of iron, manganese, zinc and copper was run using the wet method in a mixture of nitric(V) and chloric(VII) acids (3 : 1, v/v) [17]. After mineralization of plant material the following determinations were performed: N, total nitrogen using the distillation method according to Kjeldahl in a Parnas–Wagner apparatus; P, colorimetrically with ammonia molybdate; K, Ca, Mg, Na, Fe, Mn, Zn, and Cu using *atomic absorption spectroscopy* (AAS) (Carl Zeiss Jena). Results of chemical analyses of plants for their contents of macro- and microelements were analyzed statistically using the Duncan test, with inference at the significance level $\alpha = 0.05$.

Results and discussion

Growth and development of plants

The conducted statistical analysis showed a significant effect of the type and rate of fertilizer on plant height in all tested cultivars (Table 1). The application of a slow-release fertilizer with a predominant content of nitrogen Osmocote Exact Standard (16 : 11 : 11), as well as a higher rate of Osmocote Exact Hi-K (11 : 11 : 18) resulted in a stronger growth of plants. Cultivar ‘Monroe Lemon Anemone’ was an exception in this respect, in which taller plants were obtained only after the application of Osmocote Exact Hi-K (11 : 11 : 18) at 6 g · dm^{-3}. This confirms a previously stated trend for an improved growth of plants after the application of bigger rates of a slow-release fertilizer [12, 18].

In the other combinations in that cultivar no considerable effect on plant height was observed. Similar results were recorded in growing *Leucanthemum vulgare* [19] and larkspur [8]. In the other cultivars lower plants were produced under the influence of a lower rate of Osmocote Exact Hi-K (11 : 11 : 18).

Table 1

The effect of Osmocote fertilizers on the growth and flowering of marguerite daisy

Fertilizer	Height of plants [cm]		Number of inflorescences [quantity · plant^{-1}]		Number of inflorescences buds [quantity · plant^{-1}]		Diameter of inflorescences [cm]	
	Dose [g · dm^{-3}]		Dose [g · dm^{-3}]		Dose [g · dm^{-3}]		Dose [g · dm^{-3}]	
	3	6	3	6	3	6	3	6
Cultivar – Mini White Double								
Osmocote Exact Hi-K (11 : 11 : 18)	29.0a	31.5b	26.8a	29.7b	7.3ab	7.5b	3.2a	2.9a
Osmocote Exact Standard (16 : 11 : 11)	31.7b	32.5b	25.6a	30.5b	6.0a	6.0a	2.9a	2.8a
Cultivar – Monroe Lemon Anemon								
Osmocote Exact Hi-K (11 : 11 : 18)	32.6a	39.2b	31.4a	37.3b	12.0b	8.3ab	3.0ab	3.5b
Osmocote Exact Standard (16 : 11 : 11)	31.4a	31.3a	31.5a	38.6b	8.1a	10.3b	2.8a	3.4b
Cultivar – Maggy Pastel Yellow								
Osmocote Exact Hi-K (11 : 11 : 18)	40.6a	48.5b	10.5a	11.4ab	12.6bc	11.1ab	3.9ab	4.0b
Osmocote Exact Standard (16 : 11 : 11)	52.8c	50.6bc	11.2ab	12.7b	14.1c	9.6a	3.8ab	3.6a

An increase in fertilizer rates to 6 g · dm^{-3} in case of both fertilizers resulted in the formation of higher numbers of flowers on plants. According to [9] the application of Osmocote Exact flowered of Easy Pot Freesia most abundantly, regardless to cultivar.

An identical effect was also found in case of increased rates of Osmocote Plus in larkspur and in large-flowered tickseed [8, 12]. Such a dependence was not recorded in cv. ‘Maggy Pastel Yellow’, in which the type of fertilizer or its rate did not influence flowering of plants.

In the conducted experiments the type of applied fertilizer or its rate did not have a significant effect on the number of inflorescence buds or the diameter of anthodia.

Nutrient status of plants

Factors significantly modifying the state of nutrition in plants include among other things the cultivar, *ie* a genotype specific to a given cultivar [20–22], as well as applied fertilization [23–25]. The genotype of plants was a factor having a significant effect on plant nutrition with nitrogen (Table 2). The smallest mean content of this nutrient was found in cv. ‘Maggy Pastel Yellow’, while the highest in ‘Mini White Double’. The state of nitrogen nutrition in case of marguerite daisy as expressed in the mean for the tested cultivars was not influenced by the type of applied fertilizer (means for both

Table 2

The effect of Osmocote fertilizers on the content of nitrogen and phosphorus in marguerite daisy leaves

Dose (B) [g · dm^{-3}]	Fertilizer (A)								Mean for B
	Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) (A1)				Osmocote Exact Standard 3–4 M (16 : 11 : 11) (A2)				
	Cultivar (C)								
	'Mini White Double' (C1)	'Monroe Lemon Anemon' (C2)	'Maggy Pastel Yellow' (C3)	Mean for A×B	'Mini White Double' (C1)	'Monroe Lemon Anemon' (C2)	'Maggy Pastel Yellow' (C3)	Mean for A×B	
N [% in d.m.]									
3	4.69	3.85	3.15	3.90a	3.50	3.36	3.36	3.41a	3.65a
6	4.27	3.15	3.08	3.50a	3.50	3.36	3.29	3.38a	3.44a
Mean for A×C	4.48a	3.50b	3.12c		3.50a	3.36a	3.33a		
Mean for A	3.70a				3.40a				
Mean for C	C1 3.99a		C2 3.43ab			C3 3.22b			
P [% in d.m.]									
3	0.85	1.29	0.35	0.83a	1.15	1.65	0.26	1.02a	0.93a
6	0.60	1.43	0.22	0.75a	1.12	1.70	0.21	1.01a	0.88a
Mean for A×C	0.73b	1.36a	0.29c		1.14b	1.68a	0.24c		
Mean for A	0.79b				1.02a				
Mean for C	C1 0.93b		C2 1.52a				C3 0.26c		

analyzed fertilizers were similar) or their rates. In most cases a trend was observed, although not confirmed statistically, for a reduction of nitrogen content in plants with an increase in the application of this nutrient in fertilization.

There are scarce studies in available literature concerning nutrition of marguerite daisy. A closely related species, coming from the same family, is *Dendranthema grandiflora* Tzvelev (syn. *Chrysanthemum* × *grandiflorum* (Ramat.) Kitam). There are several studies concerning the nutrition of chrysanthemums [21, 22, 26–28]. Nitrogen content in leaves, recorded in this study in all the tested cultivars, was lower than the contents reported for chrysanthemums [21], amounting to 4.86–5.21 % N.

Similarly as in case of nitrogen, a significant effect of cultivar was shown on the content of phosphorus in plants (Table 2). It was lowest in case of ‘Maggy Pastel Yellow’, while it was highest for ‘Monroe Lemon Anemone’. The content of phosphorus in plants was significantly influenced also by the type of the applied fertilizer, with higher contents determined for Osmocote Exact Standard. Similarly as in case of nitrogen, a statistically unconfirmed trend could be observed for an improved state of nutrition of plants with phosphorus with an increase in the intensity of plant nutrition. For ‘Mini White Double’ and ‘Monroe Lemon Anemone’ phosphorus contents determined in plants were similar to those recorded in case of chrysanthemums [21].

The cultivar was a factor having a significant effect on the content of potassium in plants (Table 3). The highest amount of this nutrient, similarly as in case of nitrogen, was recorded in ‘Mini White Double’, while the amount was significantly lower in ‘Maggy Pastel Yellow’.

This trend was confirmed for both tested fertilizers. The type of applied slow-release fertilizer was found to have no significant effect on the state of plant nutrition with potassium. However, as it was confirmed in case of Osmocote Exact Hi-K and Osmocote Exact Standard, an increase in the intensity of nutrition increased the content of potassium in plants. Potassium content in leaves of chrysanthemums ranged from 6.48 to 7.55 % K [21], which was consistent (except for ‘Maggy Pastel Yellow’) with contents determined in this study.

Similarly as in case of the previously discussed phosphorus and potassium, a significant effect of genetic traits of a given cultivar was found on the content of calcium in plants (Table 3). For both analyzed fertilizers it was highest in cv. ‘Monroe Lemon Anemone’, while it was lowest in ‘Maggy Pastel Yellow’. Analyses showed no significant effect of the type of fertilizer or its rate on the mean content of this nutrient in plants. The above-mentioned authors [21], depending on the cultivar, recorded calcium content ranging from 2.63 to 3.10 % Ca, while in this study in cv. ‘Monroe Lemon Anemone’ its content was over 2-fold higher.

‘Monroe Lemon Anemone’ turned out to be a cultivar with a significantly highest content of magnesium, while it was lowest in ‘Mini White Double’ (Table 4).

Similarly as in case of calcium, the type of applied fertilizer and its rate were found to have no effect on significant changes in the state of magnesium nutrition in chrysanthemum. Similarly as in case of phosphorus, magnesium content determined in plants fell within a range of contents for this nutrient in chrysanthemums [21].

Table 3

The effect of Osmocote fertilizers on the content of potassium and calcium in marguerite daisy leaves

Dose (B) [g · dm^{-3}]	Fertilizer (A)								Mean for B
	Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) (A1)				Osmocote Exact Standard 3–4 M (16 : 11 : 11)				
	Cultivar (C)								
	‘Mini White Double’ (C1)	‘Monroe Lemon Anemon’ (C2)	‘Maggy Pastel Yellow’ (C3)	Mean for A×B	‘Mini White Double’ (C1)	‘Monroe Lemon Anemon’ (C2)	‘Maggy Pastel Yellow’ (C3)	Mean for A×B	
K [% in d.m.]									
3	7.91	7.07	4.32	6.43b	7.51	5.80	4.52	5.94b	6.19b
6	8.23	8.38	6.17	7.59a	7.62	7.64	5.52	6.93a	7.26a
Mean for A×C	8.07a	7.73a	5.25b		7.57a	6.72a	5.02b		
Mean for A	7.01a				6.44a				
Mean for C	C1 7.82a		C2 7.22a			C3 5.13b			
Ca [% in d.m.]									
3	4.07	7.29	2.20	4.52a	3.35	7.29	2.08	4.24a	4.38a
6	3.02	6.50	2.44	3.99a	3.51	6.83	2.52	4.29a	4.14a
Mean for A×C	3.55b	6.90a	2.32c		3.43b	7.06a	2.30c		
Mean for A	4.25a				4.26a				
Mean for C	C1 3.49b		C2 6.98a			C3 2.31c			

Table 4

The effect of Osmocote fertilizers on the content of magnesium and sodium in marguerite daisy leaves

Dose (B) [g · dm^{-3}]	Fertilizer (A)								Mean for B
	Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) (A1)				Osmocote Exact Standard 3–4 M (16 : 11 : 11)				
	Cultivar (C)								
	'Mini White Double' (C1)	'Monroe Lemon Anemon' (C2)	'Maggy Pastel Yellow' (C3)	Mean for A×B	'Mini White Double' (C1)	'Monroe Lemon Anemon' (C2)	'Maggy Pastel Yellow' (C3)	Mean for AxB	
Mg [% in d.m.]									
3	0.46	0.73	0.55	0.58a	0.45	0.73	0.52	0.57a	0.57a
6	0.40	0.67	0.56	0.54a	0.39	0.68	0.52	0.53a	0.54a
Mean for A×C	0.43c	0.70a	0.56b		0.42b	0.71a	0.52b		
Mean for A	0.56a				0.55a				
Mean for C	C1 0.43b		C2 0.70a				C3 0.54a		
Na [% in d.m.]									
3	0.91	1.10	1.23	1.08a	1.29	1.20	1.27	1.25a	1.17a
6	0.88	0.90	1.25	1.01a	1.06	1.00	1.31	1.12a	1.07a
Mean for A×C	0.90b	1.00b	1.24a		1.18a	1.10b	1.29a		
Mean for A	1.05a				1.19a				
Mean for C	C1 1.04b		C2 1.05b					C3 1.27a	

In the conducted experiments significant changes were shown in the content of sodium depending on the cultivar (Table 4). The lowest amount of this ion was found in 'Mini White Double', while it was highest in 'Maggy Pastel Yellow'. No significant effect of fertilizer rates or its type was observed on the content of sodium in plants. In turn, the contents of sodium as a ballast ion, not being a nutrient, were almost 10 times higher than those reported previously [21].

Specific genetic traits of tested cultivars turned out to a factor significantly modifying the content of metallic microelements such as iron, manganese, zinc and copper in plants. The highest amounts of iron and manganese were determined in 'Monroe Lemon Anemone', while the lowest amounts of these nutrients were recorded in 'Maggy Pastel Yellow' (Table 5).

The type of the applied fertilizer had a significant effect on iron content, at the same time having no modifying effect on the content of manganese in plants. For the mean of the tested combinations no significant effect of the rate of fertilizer was found for plant nutrition with iron and manganese. For iron a significant variation was observed between cultivars. Determined contents of this nutrient ranged in case of the 2 tested cultivars fell within the range given above, *ie* from 121.5 to 169.5 mg $\cdot$ kg^{-1} d.m. [21, modif.]. In other studies [22] in chrysanthemum leaves the levels ranged from 69.17 to 193.07 mgFe $\cdot$ kg^{-1} d.m.. Similar contents of this nutrient to those recorded in this study are reported in literature [26, 27]. The contents of manganese determined in plants in this study were markedly higher than the range of contents for this nutrient reported by Jerzy et al [21], amounting to 48.0–85.0 mg.

'Monroe Lemon Anemone' was a cultivar with significantly highest content of zinc, while it was lowest in 'Maggy Pastel Yellow' (Table 6). The above-mentioned dependence was found in case of both tested fertilizers. No effect of the type of fertilizer on the content of this nutrient in plants was observed, at the simultaneous positive effect of the applied rates. The content of zinc in plants increased significantly with an increase in the intensity of nutrition.

Similarly as in case of iron, manganese and zinc, a significant effect of specific cultivar traits was found on the content of copper in plants (Table 6). It was significantly highest in 'Maggy Pastel Yellow', while it was lower in case of the other cultivars. The type of applied fertilizer had no significant effect on the state of nutrition of plants with this microelement.

Adaptation of nutrition to species-specific or even cultivar-specific requirements is one of the factors influencing yielding of plants, both quantitatively and qualitatively. This may be provided by the determination of nutrients guide values (content of nutrients in plants), at which optimal yielding is achieved. Guide values are thus a valuable diagnostic tool in controlled plant nutrition. Their determination is particularly important in species with an increasing importance in commercial cultures, which group includes also marguerite daisy. Guide values for individual cultivars are as follows:

– 'Mini White Double' [in % d.m.]: N 3.50–4.27, P 0.60–1.12, K 7.62–8.23, Ca 3.02–3.51, Mg 0.42–0.43; [in mg $\cdot$ kg^{-1} d.m.]: Fe 114.0–160.3, Mn 334.1–339.5, Zn 69.1–76.8, Cu 5.2–5.4,

Table 5

The effect of Osmocote fertilizers on the content of iron and manganese in marguerite daisy leaves

Dose (B) [g · dm^{-3}]	Fertilizer (A)								Mean for B
	Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) (A1)				Osmocote Exact Standard 3–4 M (16 : 11 : 11)				
	Cultivar (C)								
	‘Mini White Double’ (C1)	‘Monroe Lemon Anemon’ (C2)	‘Maggy Pastel Yellow’ (C3)	Mean for A×B	‘Mini White Double’ (C1)	‘Monroe Lemon Anemon’ (C2)	‘Maggy Pastel Yellow’ (C3)	Mean for A×B	
Fe [mg · kg^{-1}]									
3	153.1	221.7	130.6	168.5a	154.0	280.4	120.1	184.8a	176.7a
6	74.9	351.7	125.1	183.9a	166.5	318.9	132.4	205.9a	194.9a
Mean for A×C	114.0b	286.7a	127.9b		160.3b	299.7a	126.3b		
Mean for A	176.2a				195.4b				
Mean for C	C1 137.1a		C2 293.2b			C3 127.1a			
Mn [mg · kg^{-1}]									
3	305.4	358.6	210.9	291.6b	329.9	477.5	304.5	370.6a	331.1a
6	362.7	477.9	285.8	375.5a	349.1	411.7	289.6	350.1a	362.8a
Mean for A×C	334.1b	418.3a	248.4c		339.5b	444.6a	297.1c		
Mean for A	333.6a				360.4a				
Mean for C	C1 336.8b		C2 431.4 a				C3 272.7c		

Table 6

The effect of Osmocote fertilizers on the content of zinc and copper in marguerite daisy leaves

Dose (B) [g · dm^{-3}]	Fertilizer (A)								Mean for B
	Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) (A1)				Osmocote Exact Standard 3–4 M (16 : 11 : 11)				
	Cultivar (C)								
	‘Mini White Double’ (C1)	‘Monroe Lemon Anemon’ (C2)	‘Maggy Pastel Yellow’ (C3)	Mean for A×B	‘Mini White Double’ (C1)	‘Monroe Lemon Anemon’ (C2)	‘Maggy Pastel Yellow’ (C3)	Mean for A×B	
Zn [mg · kg^{-1}]									
3	70.1	68.2	22.8	53.7b	76.7	87.9	6.6	57.1b	55.4b
6	68.0	113.2	31.0	70.7a	76.8	109.1	30.8	72.2a	71.5a
Mean for A×C	69.1	90.7	26.9	62.2	76.8	98.5	18.7	69.1	
Mean for A	62.2a				64.7a				
Mean for C	C1 72.9b		C2 94.6a			C3 22.8c			
Cu [mg · kg^{-1}]									
3	4.8	5.6	8.1	6.2a	4.4	5.3	5.4	5.0a	5.6a
6	5.4	5.7	5.3	5.5a	5.2	4.5	5.8	5.2a	5.3a
Mean for A×C	5.1b	5.7b	6.7a		4.8b	4.9b	5.6a		
Mean for A	5.8a				5.1a				
Mean for C	C1 5.0b			C2 5.3b			C3 6.2a		

– ‘Monroe Lemon Anemon’ [n % d.m.]: N 3.15–3.36, P 1.43–1.70, K 7.64–8.38, Ca 6.50–6.83, Mg 0.70–0.71; [in mg $\cdot$ kg^{-1} d.m.]: Fe 286.7–299.7, Mn 418.3–444.6, Zn 90.7–98.5, Cu 4.5–5.7,

– ‘Maggy Pastel Yellow’ [in % d.m.]: N 3.08–3.29, P 0.21–0.22, K 5.52–6.17, Ca 2.44–2.52, Mg 0.52–0.56; [in mg $\cdot$ kg^{-1} d.m.]: Fe 126.3–127.9, Mn 248.4–297.1, Zn 18.7–26.9, Cu 5.3–5.8.

Taking into consideration the trend for the improvement of plant quality, expressed in their height as well as the number and diameter of flowers, in pot culture of different cultivars of marguerite daisy from Molimba® group the tested slow-release fertilizers Osmocote Exact Hi-K 3–4 M and Osmocote Exact Standard 3–4 M may be recommended at a rate of 6 g $\cdot$ dm^{-3} substrate. Their use is advantageous due to the significant simplification of cultivation and a limitation of the potential environmental hazard as a result of drainage waters leaking to the soil.

Conclusions

On the basis of conducted studies on the application of slow-release fertilizers Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) and Osmocote Exact Standard 3–4 M (16 : 11 : 11) in pot culture of Molimba® group marguerite daisy the following may be stated:

1. The application of slow-release fertilizer with the predominant content of nitrogen Osmocote Exact Standard (16 : 11 : 11), as well as a higher rate of Osmocote Exact Hi-K (11 : 11 : 18) resulted in a stronger growth of plants. ‘Monroe Lemon Anemone’ was an exception in this respect.
2. In cv. ‘Mini White Double’ and ‘Monroe Lemon Anemone’ more abundantly flowering plants were produced under the influence of higher rates of slow-release fertilizers.
3. The type of fertilizer, as well as its rate had no significant effect on the number of inflorescence buds or the diameter of anthodia.
4. The cultivar significantly modified the contents of both macro- and microelements in plants.
5. A significantly better nutrition of plants with phosphorus and iron was shown after the application of Osmocote Exact Standard 3–4 M (16 : 11 : 11). Differences in the contents of the other macro- and microelements in plants found between the tested fertilizers were non-significant.
6. An increase in the rates of Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) had a significant effect on the state of nutrition of plants with potassium, manganese and zinc, while in case of Osmocote Exact Standard 3–4 M (16 : 11 : 11) it was for potassium and zinc.
7. The following ranges of guide values, at which yielding of plants was most advantageous, are proposed for individual cultivars:

– ‘Mini White Double’ [in % d.m.]: N 3.50–4.27, P 0.60–1.12, K 7.62–8.23, Ca 3.02–3.51, Mg 0.42–0.43; [in mg $\cdot$ kg^{-1} d.m.]: Fe 114.0–160.3, Mn 334.1–339.5, Zn 69.1–76.8, Cu 5.2–5.4,

– ‘Monroe Lemon Anemone’ [in % d.m.]: N 3.15–3.36, P 1.43–1.70, K 7.64–8.38, Ca 6.50–6.83, Mg 0.70–0.71; [in mg $\cdot$ kg^{-1} d.m.]: Fe 286.7–299.7, Mn 418.3–444.6, Zn 90.7–98.5, Cu 4.5–5.7,

– ‘Maggy Pastel Yellow’ [in % d.m.]: N 3.08–3.29, P 0.21–0.22, K 5.52–6.17, Ca 2.44–2.52, Mg 0.52–0.56; [in mg · kg^{-1} d.m.]: Fe 126.3–127.9, Mn 248.4–297.1, Zn 18.7–26.9, Cu 5.3–5.8.

8. Taking into consideration both the practical aspect, consisting in the simplification of cultivation methods in commercial production, and the quality of plants, and the ecological aspect, *ie* the potential reduction of nutrient leaching hazardous for the natural environment outside the root zone to groundwater, the tested slow-release fertilizers are suitable for the growing of Molimba® group marguerite daisy.

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ZASTOSOWANIE NAWOZÓW O SPOWOLNIONYM DZIAŁANIU W UPRAWIE SREBRZENIA KRZEWIASTEGO (*Argyranthemum frutescens*) Z GRUPY Molimba

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Abstrakt: Celem przeprowadzonych badań była ocena wpływu stosowania nawozów o spowolnionym działaniu: Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) oraz Osmocote Exact Standard 3–4 M (16 : 11 : 11) na wzrost i kwitnienie 3 odmian srebrzenia krzewiastego (*Argyranthemum frutescens)* z grupy Molimba. Oceniano wysokość roślin, liczbę pąków kwiatostanowych, liczbę i średnicę koszyczków kwiatowych, a także stan odżywienia roślin makro i mikroelementami. W wyniku przeprowadzonego doświadczenia stwierdzono, że w zależności od odmiany zarówno typ, jak i dawka zastosowanego nawozu wpływała na wysokość roślin. Zastosowanie nawozu o spowolnionym działaniu z przewagą azotu Osmocote Exact Standard (16 : 11 : 11), a także wyższej dawki Osmocote Exact Hi-K (11 : 11 : 18) spowodowało silniejszy wzrost roślin. Wyjątek stanowiła odmiana 'Monroe Lemon Anemon'. U odmiany 'Mini White Double' i 'Monroe Lemon Anemon' obficiej kwitnące rośliny uzyskano pod wpływem wyższych dawek nawozów o spowolnionym działaniu. Typ nawozu, a także jego dawka nie miała istotnego wpływu na liczbę pąków kwiatostanowych, a także średnicę koszyczków kwiatowych. Odmiana istotnie modyfikowała zarówno zawartości makro, jak i mikroelementów w roślinach. Wykazano istotnie lepsze odżywienie roślin fosforem i żelazem po zastosowaniu Osmocote Exact Standard 3–4 M (16 : 11 : 11) w porównaniu z Osmocote Exact Hi-K. Różnice zawartości pozostałych makro i mikroelementów w roślinach występujące pomiędzy badanymi nawozami nie były istotne. Wzrost dawki nawozu Osmocote Exact Hi-K 3–4 M (11 : 11 : 18) wpływał istotnie na stan odżywienia roślin potasem, manganem i cynkiem – a w przypadku Osmocote Exact Standard 3–4 M (16 : 11 : 11) potasem i cynkiem. Biorąc pod uwagę aspekt praktyczny, polegający na uproszczeniu metod uprawy w warunkach produkcyjnych, jak również jakość roślin oraz aspekt proekologiczny – ograniczenia niebezpiecznego dla środowiska naturalnego wymywania składników pokarmowych poza strefę korzeniową roślin do wód gruntowych, badane nawozy wolnodziałające są przydatne do uprawy srebrzenia krzewiastego z grupy Molimba.

Słowa kluczowe: nawozy o spowolnionym działaniu, wzrost, stan odżywienia, analizy roślin

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EFFECT OF ORGANIC FERTILISATION WITHOUT AND WITH ADDITION OF ACTIVATING SUBSTANCE PRP Sol ON SOME SOIL FERTILITY INDICES

WPŁYW NAWOŻENIA ORGANICZNEGO BEZ I Z DODATKIEM SUBSTANCJI AKTYWUJĄCEJ PRP Sol NA NIEKTÓRE WSKAŹNIKI ŻYZNOŚCI GLEBY

Abstract: A field experiment was carried out at the Agricultural Experimental Station in Lipnik in 2008–2009 on the soil belonging to soil quality class IV_a and good rye agricultural suitability complex (5). The compost applied in this study was produced by the GWDA method at the Municipal Sewage Treatment Plant in Stargard Szczecinski. It was characterised by neutral reaction (pH_{H_2O} 7.15). The total content of macroelements and heavy metals, which limits the possibility of using it for fertilisation purposes, did not exceed the standards specified in the Regulation of the Minister of Agriculture and Rural Development [Official Journal of Laws of 2008 No. 119, item 765]. Compost doses were established based on total nitrogen content. The experiment was conducted with two rotations without and with addition of active substance PRP Sol. In autumn 2007, respective compost doses were introduced into soil in the designated experimental plots according to the study design. Active substance PRP Sol was introduced into soil at a dose of 150 $kgN \cdot ha^{-1}$ before sowing or planting the test plants. In 2008 and 2009, the whole experimental area was fertilised with multicomponent fertiliser Polifoska 6 at a dose of 200 $kg \cdot ha^{-1}$ and urea (46 % N), as topdressing, at a dose of 100 $kgN \cdot ha^{-1}$. Test plants were winter wheat of the cultivar *Korweta* in 2008 and spring rape of the cultivar *Bosman* in 2009.

The activating substance PRP Sol being applied against the control object and those with increasing doses of municipal sewage sludge compost did not significantly affect an increase in the total content of macroelements in soil but contributed to an average increase in the content of phosphorus, potassium, magnesium and sulphur in soil by 26.6 %, 4.84 %, 21.7 % and 38.9 %, respectively, when compared with that before setting up this experiment. The average content of assimilable nutrients in soil in the objects being fertilised with increasing doses of municipal sewage sludge compost without and with addition of activating

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substances PRP Sol in case of phosphorus and potassium was very high and high, which means that an increase occurred in soil abundance by one class.

Keywords: municipal sewage sludge, compost, activating substance PRP Sol, soil, total and assimilable phosphorus, potassium, magnesium and sulphur contents

Introduction

Sharp increase in mineral fertiliser prices has contributed to acquisition of new and cheap sources of organic matter and nutrients for plants. Therefore, organic and organic-mineral substances are being applied to determine their effect on soil fertility indices and plant yield quantity and quality as well as their environmental impact.

Municipal sewage sludge and composts being produced from it are a source of organic matter and some macroelements [1–11]. Therefore, they are characterised by high manurial value and it is recommended to apply them as organic fertilisers to enrich soil [12–17]. They must, however, meet the standards specified in the Regulation of the Minister of Environment [18] to have no negative environmental impact. Numerous studies indicate that they have a favourable effect on relationships between the "soil culture" and its chemical and physical properties and biological activity [19–21].

Activating substance PRP Sol pellet is composed of 30 % CaO, 8 % MgO, 3.5 % Na and 3–5 % premixes, with which 48 microelements is being introduced into soil (among others manganese, lead, iron, boron, and molybdenum). The content of respective PRP Sol components contributes to, among others, improving soil physical properties, induces the conversion of sparingly available phosphorus, potassium and magnesium into compounds that can be available for plants, and enriches the soil with microelements necessary for plant development [22–23].

Composts produced from municipal sewage sludge being used for soil fertilisation may improve the environmental balance of organic matter and nutrients. Reaction changes have an effect on the activation or retrogradation of many nutrients in soil necessary for plants. Therefore, it is reasonable to carry out research on the effect of composts with activating substance PRP Sol addition on physicochemical changes in mineral soils.

The carried out study aimed at determination of the effect of fertilisation with increasing doses of organic fertiliser without and with addition of active substance PRP Sol on total and assimilable phosphorus, potassium, magnesium and sulphur contents in soil during a 2-year study period.

Material and research methods

The Agricultural Experimental Station (AES) in Lipnik is situated on complete and incomplete brown acid soils (soil quality class V and IVa and IVb, respectively). A field experiment was set up and conducted at this station. The soil on which this field experiment was carried out at the AES in Lipnik is included among incomplete brown soils, formed from silty light loamy sand, with a medium deeply underlying layer of sandy loam. It belongs to soil quality class IVa and good rye agricultural suitability complex (5). The carried out examination of arable layer soil (0–25 cm) showed that assimilable phosphorus richness of that soil was high (78.2 mg $\cdot$ kg^{-1} d.m.), while that of potassium and magnesium was average (113.9 and 38.6 mg $\cdot$ kg^{-1} d.m, respectively). This soil was characterised by a reaction similar to the neutral one (pH$_{KCl}$ 6.65), its organic carbon content amounted to 7.55, while that of nitrogen, phosphorus, potassium, calcium, magnesium and sulphur to 0.64, 1.10, 2.41, 2.18, 0.60 and 0.12 g $\cdot$ kg^{-1} d.m., respectively.

The municipal sewage sludge compost applied in this experiment was produced by the GWDA method at the Municipal Sewage Treatment Plant in Stargard Szczeciński. It was characterised by neutral reaction (pH$_{H_2O}$ 7.15) and contained more nitrogen and phosphorus (28.6 and 12.0 g $\cdot$ kg^{-1} d.m., respectively) when compared with potassium (6.70 g $\cdot$ kg^{-1} d.m.). The magnesium content was 2.22 g $\cdot$ kg^{-1} d.m., while that of calcium 4.80 g $\cdot$ kg^{-1} d.m. The carbon-to-nitrogen ratio amounted to 8.60 and was slightly narrowed. The total content of heavy metals, which limits the possibility of using it for fertilisation purposes, did not exceed the standards specified in the Regulation of the Minister of Agriculture and Rural Development [18].

Test plants in the experiment being conducted were winter wheat of the cultivar *Korweta* in 2008 and spring rape of the cultivar *Bosman* in 2009. This experiment included two factors: factor A – increasing compost doses, and factor B – increasing compost + PRP Sol doses. A control was the object without fertilisation (control I) and that with addition of active substance PRP Sol (control II). The study design included three doses of municipal sewage sludge compost. The size of compost dose was determined at a level corresponding to 100, 200 and 300 kgN $\cdot$ ha^{-1}, respectively.

In autumn 2007, respective compost doses were introduced into soil in the designated experimental plots according to the study design. In March 2008 and 2009, the whole experimental area was fertilised with multicomponent fertiliser Polifoska 6 at a dose of 200 kg $\cdot$ ha^{-1}. Due to low nitrogen content in multicomponent fertiliser Polifoska 6 (6 % N), additional nitrogen fertilisation was applied in the form of urea (46 % N) as the topdressing at a dose of 100 kgN $\cdot$ ha^{-1}. The total dose of nitrogen under spring rape and winter wheat was divided into two equal parts, applying them at two times (spring – 50 % of this dose before sowing spring rape and 50 % of it before inter-row spacing, and 50 % at the start of vegetation under winter wheat and 50 % in the shooting stage). Active substance PRP Sol was introduced into soil at a dose of 150 kgN $\cdot$ ha^{-1} before sowing the test plants. In autumn 2008 and 2009, the same agrotechnical measures were performed in the field experiment being carried out. Soil samples for chemical analyses were collected from the arable layer (0–25 cm) each year after completion of the vegetation period. In the soil being examined, total and assimilable phosphorus, potassium, magnesium and sulphur contents were determined. Each year, after harvesting test plant, the content of macroelements was determined in soil in averaged samples from four replications for each fertilisation object. Sulphur contents were determined on a Coestech CNS elemental analyser, while that of assimilable phosphorus and potassium forms by the Egner-Riehm method, assimilable magnesium content according to the Polish standard PN-R-04024, total phosphorus content according to the Polish standard PN-98/C-04537-14, total potassium content by the method of flame photometry content by the method of *atomic absorption spectrometry* (AAS) on a Perkin Elmer AAS 300 spectrometer, sulphur and sulphate nephelometric method. The stock solution was obtained after previous wet mineralisation of soil material according to the Polish standards PN-ISO 11466 and PN-ISO 11047.

Total contents of assimilable of macroelements was processed statistically by the analysis of variance method using Statistica 8.0 PL computer software package. In case of significant differences, the Tukey's test was used at significance level $p = 0.05$.

Results and discussion

After completion of two-year study, some soil fertility properties were determined in average samples of each experimental object. Study results are presented in Tables 1 and 2 and Fig. 1 and 2. The findings are compared with the results of examinations being performed before starting the experiment.

Total phosphorus, potassium, magnesium and sulphur contents in soil in the control object after two years of experiment were smaller than or equal to those before starting the study (Table 1). Introduction of the first dose of municipal sewage sludge compost into soil induced an increase in phosphorus, potassium, magnesium and sulphur contents by 12.9 %, 5.43 %, 11.7 % and 8.33 %, respectively, while increased slightly the total content of macroelements in soil when compared with the control. Application of the second and the third dose of municipal sewage sludge compost induced a slight increase in the content of chemical elements being discussed in soil when compared with the first dose. Significant effect of organic fertilisation was observed in the increased total phosphorus and magnesium contents in soil.

The total contents of chemical elements under discussion in soil in the fertilisation objects with increasing doses of municipal sewage sludge compost with addition of active substance PRP Sol were higher than before setting up this experiment. Sewage sludge and composts being produced from it are abundant with phosphorus and therefore the content of that chemical element in the humus horizon of soil increases after their application. According to Grzywanowicz [24] and Czekala [25], this increase may be persist in the first year as well as in the next years after application of organic fertilisation. Wojcikowska-Kapusta et al [26] suggest that possibility of total phosphorus accumulation in soil should be taken into account. This phenomenon is induced by high calcium and magnesium contents in compost, which affects not only the pH_{KCl} value but also the formation of sparingly soluble phosphorus compounds. The obtained drops in assimilable potassium content in soil are associated with low content of that chemical element in sewage sludge and composts produced from it [1, 25, 27].

The activating substance PRP Sol being applied against the control object and that with increasing doses of municipal sewage sludge compost did not significantly affect an increase in the total content of macroelements in soil but contributed to an average increase in the content of phosphorus, potassium, magnesium and sulphur in soil by 26.6 %, 4.84 %, 21.7 % and 38.9 %, respectively, when compared with that before setting up this experiment (Table 1).

Table 1

Effect of increasing doses of municipal sewage sludge compost and activating substance PRP Sol on total phosphorus, potassium, magnesium and sulphur contents in soil after completion of the experiment

Fertilisation variants	Years	Total content [$g \cdot kg^{-1}$ d.m.]			
		P	K	Mg	S
Initial values		**1.10**	**2.41**	**0.60**	**0.12**
I dose of compost without PRP Sol	2008	1.21	2.60	0.64	0.13
	2009	1.34	2.45	0.71	0.14
Mean		**1.27**	**2,52**	**0.67**	**0.13**
II dose of compost without PRP Sol	2008	1.28	2.68	0.68	0.14
	2009	1.34	2.51	0.73	0.15
Mean		**1.31**	**2.59**	**0.70**	**0.14**
III dose of compost without PRP Sol	2008	1.32	2.52	0.71	0.16
	2009	1.39	2.60	0.76	0.20
Mean		**1.35**	**2.56**	**0.73**	**0.18**
I dose of compost with PRP Sol	2008	1.34	2.45	0.65	0.13
	2009	1.38	2.49	0.75	0.15
Mean		**1.36**	**2.47**	**0.70**	**0.14**
II dose of compost with PRP Sol	2008	1.39	2.48	0.70	0.15
	2009	1.41	2.55	0.75	0.17
Mean		**1.40**	**2.51**	**0.72**	**0.16**
III dose of compost with PRP Sol	2008	1.41	2.53	0.75	0.18
	2009	1.44	2.68	0.80	0.22
Mean		**1.42**	**2.60**	**0.77**	**0.20**
Control	2008	1.12	2.38	0.60	0.11
	2009	1.15	2.40	0.62	0.13
Mean		**1.13**	**2.39**	**0.61**	**0.12**
Control with PRP Sol	2008	1.18	2.42	0.66	0.14
	2009	1.20	2.44	0.68	0.15
Mean		**1.19**	**2.43**	**0.67**	**0.14**
$LSD_{0.05}$ A – compost doses B – PRP Sol fertilisation A × B		 0.06 n.s.* n.s.	 n.s. n.s. n.s.	 0.05 n.s. n.s.	 n.s. n.s. n.s.

* n.s. – non-significant.

The content of plant-assimilable phosphorus, potassium and magnesium in soil from the control object, as well as that of sulphate sulphur, was lower than their contents before starting the study (Table 2 and Fig. 1).

Table 2

The effect of increasing doses of municipal sewage sludge compost and activating substance PRP Sol on assimilable phosphorus, potassium, magnesium and sulphate sulphur contents in soil after completion of the experiment

Fertilisation variants	Years	Content assimilable [g $\cdot$ kg^{-1} d.m.]			
		P	K	Mg	S
Initial values		**78.2**	**113.9**	**38.6**	**9.26**
I dose of compost without PRP Sol	2008	103.4	125.9	42.7	9.85
	2009	89.9	115.2	54.9	10.3
Mean		**96.6**	**120.2**	**48.8**	**10.1**
II dose of compost without PRP Sol	2008	110.6	137.6	46.6	9.98
	2009	92.5	119.0	54.2	10.2
Mean		**101.5**	**128.3**	**49.9**	**10.4**
III dose of compost without PRP Sol	2008	120.4	141.7	48.3	10.8
	2009	100.0	122.5	53.5	12.1
Mean		**110.2**	**132.1**	**50.9**	**11.5**
I dose of compost with PRP Sol	2008	115.0	145.5	43.1	9.90
	2009	102.0	125.7	56.1	10.7
Mean		**108.5**	**135.6**	**49.6**	**10.3**
II dose of compost with PRP Sol	2008	119.7	149.3	47.8	10.9
	2009	110.5	133.9	54.8	11.4
Mean		**115.1**	**141.6**	**51.3**	**11.2**
III dose of compost with PRP Sol	2008	124.6	147.1	49.9	11.6
	2009	115.6	138.5	53.7	12.0
Mean		**120.1**	**142.8**	**51.8**	**11.8**
Control	2008	75.6	112.3	36.1	8.90
	2009	74.4	111.9	39.0	9.00
Mean		**75.0**	**112.1**	**36.5**	**8.96**
Control with PRP Sol	2008	84.1	114.9	37.2	9.18
	2009	84.9	114.1	37.8	9.22
Mean		**84.5**	**114.5**	**37.5**	**9.20**
LSD$_{0.05}$					
A – compost doses		12.3	13.1	7.21	0.68
B – PRP Sol fertilisation		6.23	6.30	n.s.*	0.34
A × B		n.s.	n.s.	n.s.	n.s

* n.s. – non-significant.

Introduction of the first dose of municipal sewage sludge compost induced an increase in the content of plant-assimilable phosphorus, potassium, magnesium and sulphate sulphur in soil when compared with the control object. The content of plant-assimilable macroelements increased by 21.6, 8.1, 12.3 and 1.14 mg $\cdot$ kg^{-1} d.m.,

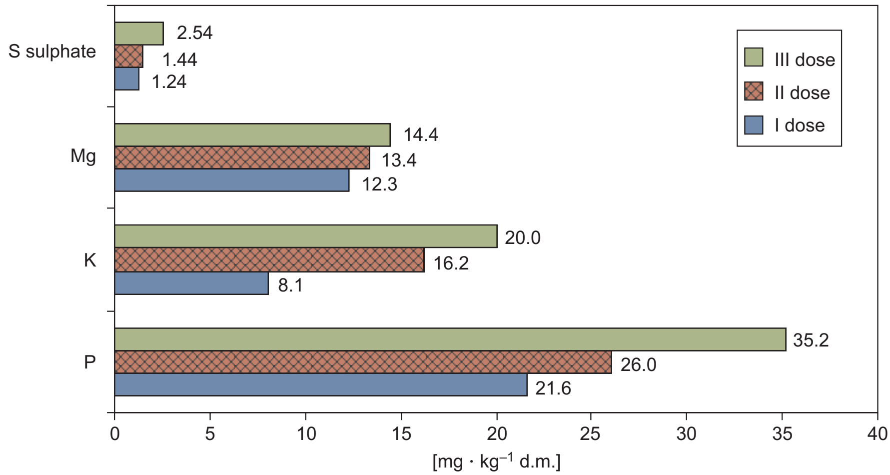

Fig. 1. Increase in plant-assimilable phosphorus, potassium, magnesium and sulphate sulphur contents in soil obtained as affected by increasing doses of municipal sewage sludge compost after completion of the study

respectively, for phosphorus, potassium, magnesium and sulphate sulphur. Similar effect was obtained after introduction of the second dose of municipal sewage sludge compost; assimilable phosphorus, potassium, magnesium and sulphate sulphur contents increased, respectively, by 26.5, 16.2, 13.4 and 1.44 mg · kg^{-1} d.m. soil when compared with the control object. Fertilisation with the third dose of municipal sewage sludge compost induced a further increase (as compared with the control object) in plant-assimilable phosphorus, potassium, magnesium and sulphate sulphur contents by 35.2, 20.0, 14.4 and 2.54 mg · kg^{-1} d.m. soil, respectively (Fig. 2).

Significant increase in the content of plant-assimilable phosphorus, potassium, magnesium and sulphur was observed in the fertilisation objects with exclusive application of organic fertilisation. The activating substance PRP Sol being introduced into soil contributed to a significant increase in potassium, phosphorus and sulphur contents in soil.

Summing up, it is possible to state that the content of plant-assimilable phosphorus in soil increased to the greatest extent after application of municipal sewage sludge compost (by 37 %),followed by that of magnesium (by 36.7 %), sulphate sulphur (by 19.5 %) and potassium (by 13.2 %), when compared with the control object (Table 2). These results show that plant-assimilable phosphorus and potassium forms had been introduced into soil together with municipal sewage sludge compost. Part of the plant-assimilable phosphorus and potassium forms could have also come from further decomposition of the composting mass in soil. The obtained results find their confirmation in the studies indicating a possibility of using municipal sewage sludge for fertilisation purposes [24, 28–32]. On the other hand, the activating substance PRP Sol being applied against the control object and the increasing compost doses increased the content of plant-assimilable phosphorus and potassium in soil in the study by Bourguignon [32].

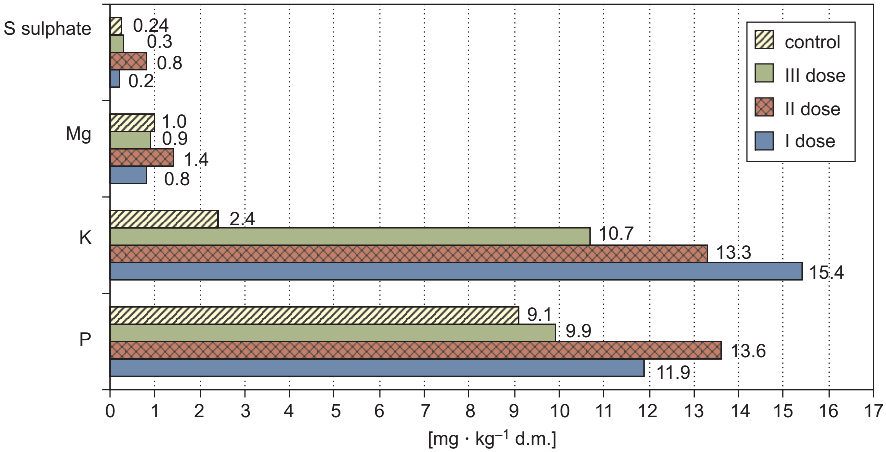

Fig. 2. The effect of activating substance PRP Sol being applied in the control object and those fertilised with increasing doses of municipal sewage sludge compost on the increase in plant-assimilable phosphorus, potassium, magnesium and sulphate sulphur contents in soil. Data are given in mg · kg^{-1} d.m.

Based on the data given in Table 2, the effect of activating substance PRP Sol being applied in the control object and in those fertilised with increasing doses of municipal sewage sludge compost on plant-assimilable phosphorus, potassium, magnesium and sulphate sulphur contents in soil was estimated. Results of these calculations are presented in Fig. 2.

The application of activating substance PRP Sol in the control object and in those being fertilised with increasing dosed of municipal sewage sludge compost affected an increase in plant assimilable phosphorus, potassium, magnesium and sulphate sulphur concentrations in soil. The content of plant-assimilable phosphorus in soil increased to the greatest extent (on average by 11.1 mgP · kg^{-1} d.m. soil), followed by that of potassium (on average by 10.4 mgK · kg^{-1} d.m. soil), magnesium (on average by 1.02 mgMg · kg^{-1} d.m. soil) and sulphate sulphur (on average by 0.38 mgS-SO$_4$ · kg^{-1} d.m. soil) – see Fig. 2.

When evaluating the average content of assimilable nutrients in soil with the method of threshold limit values used by Chemical and Agricultural Research Laboratories, it was found that assimilable phosphorus and potassium contents were very high and high in the objects being fertilised with increasing doses of municipal sewage sludge compost without and with addition of active substance PRP Sol, which means that an increase occurred in soil abundance by one class. The content of assimilable magnesium in soil was medium, which means that no changes in soil abundance class were observed.

Conclusions

1. Application of a single dose of municipal sewage sludge compost induced an increase in phosphorus, potassium, magnesium and sulphur contents in soil. Application

of the second and the third dose of municipal sewage sludge compost contributed to a slight increase in the content of chemical elements under discussion in soil when compared with the first dose. Significant effect of organic fertilisation was only observed in an increase in phosphorus and magnesium contents in soil.

2. The activating substance PRP Sol being applied against the control object and those with increasing doses of municipal sewage sludge compost did not significantly affect an increase in the total content of macroelements in soil.

3. Significant increase in the content of plant-assimilable phosphorus, potassium, magnesium and sulphur was observed in the fertilisation objects with exclusive application of organic fertilisation. The activating substance PRP Sol being introduced into soil contributed to a significant increase in potassium, phosphorus and sulphur contents in soil.

4. The content of plant-assimilable phosphorus content in soil increased to the greatest extent after application of municipal sewage sludge compost, followed by that of magnesium, sulphate sulphur and potassium, when compared with the control object.

5. When evaluating the average content of assimilable nutrients in soil with the method of threshold limit values, it was found that assimilable phosphorus and potassium contents were very high and high in the objects being fertilised with increasing doses of municipal sewage sludge compost without and with addition of active substance PRP Sol, which means that an increase occurred in soil abundance by one class.

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WPŁYW NAWOŻENIA ORGANICZNEGO BEZ I Z DODATKIEM SUBSTANCJI AKTYWUJĄCEJ PRP Sol NA NIEKTÓRE WSKAŹNIKI ŻYZNOŚCI GLEBY

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Abstrakt: Doświadczenie polowe przeprowadzono w latach 2008–2009 na terenie RSD w Lipniku na glebie zaliczanej do klasy bonitacyjnej IV$_a$, kompleksu przydatności rolniczej żytniego dobrego (5). Do badań użyto kompostu wyprodukowanego w Komunalnej Oczyszczalni Ścieków w Stargardzie Szczecińskim. Charakteryzował się odczynem obojętnym (pH_{H_2O} 7.15). Zawartość ogólna makroskładników i metali ciężkich, która limituje możliwość wykorzystania go do celów nawozowych nie przekraczała norm podanych w Rozporządzeniu Ministra Rolnictwa i Rozwoju Wsi [DzU 08.119.765]. Dawki kompostu ustalono na podstawie zawartości azotu ogólnego. Doświadczenie prowadzono w dwóch rotacjach bez i z dodatkiem substancji aktywnej PRP Sol. Jesienią 2007 r. zgodnie ze schematem badań na wyznaczonych poletkach wprowadzono do gleby odpowiednie dawki kompostu. Substancję czynną PRP Sol w dawce 150 kg $\cdot$ ha^{-1} stosowano przed siewem lub sadzeniem roślin testowych. Całą powierzchnię doświadczenia w 2008 i 2009 roku nawożono Polifoską 6 w dawce 200 kg $\cdot$ ha^{-1} oraz pogłównie w formie mocznika (46 % N) w dawce 100 kgN $\cdot$ ha^{-1}. Roślinami testowymi były: w 2008 roku pszenica ozima odmiany *Korweta,* a 2009 rzepak jary odmiany *Bosman*.

Substancja aktywująca PRP Sol stosowana na tle obiektów: kontrolnego oraz ze wzrastającymi dawkami kompostu z komunalnego osadu ściekowego nie miała istotnego wpływu na zwiększenie form ogólnych makroskładników w glebie, ale przyczyniła się do średniego wzrostu w glebie zawartości fosforu o 26.6 %, potasu o 4.84 %, magnezu o 21.7 % i siarki o 38.9 % w porównaniu do zawartości sprzed założenia doświadczenia. Średnią zawartość składników przyswajalnych w glebie na obiektach nawożonych wzrastającymi dawkami kompostu bez i z dodatkiem substancji aktywującej PRP Sol fosforu i potasu przyswajalnego była bardzo wysoka i wysoka, co oznacza, że nastąpił wzrost zasobności gleby o jedną klasę.

Słowa kluczowe: komunalny osad ściekowy, kompost, substancja czynna PRP Sol, gleba, zawartość ogólna i form przyswajalnych fosforu, potasu, magnezu i siarki

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EFFECT OF SPRING BARLEY NITROGEN FERTILISATION ON THE CHANGES IN THE CONTENT OF PHOSPHORUS AND THE ACTIVITY OF ALKALINE AND ACID PHOSPHATASE IN SOIL

WPŁYW NAWOŻENIA AZOTEM JĘCZMIENIA JAREGO NA ZMIANY ZAWARTOŚCI FOSFORU I AKTYWNOŚCI FOSFATAZY ALKALICZNEJ I KWAŚNEJ W GLEBIE

Abstract: The aim of the present paper was to determine changes in the content of available phosphorus and the activity of alkaline and acid phosphatase as a result of nitrogen fertilisation at the following rates: 0, 30, 60, 90, 120, 150 kgN · ha^{-1} and mineral fertilisation (P, K, Mg, Ca and S) in soil under spring barley. The soil was sampled in June and October 2008 from a field experiment set up in the area of the Agricultural Experiment Station at Grabow on the Vistula, by the Institute of Soil Science and Plant Cultivation (IUNG) in Pulawy. There was found a significant effect of nitrogen fertilisation on the content of available phosphorus in the soil. High nitrogen rates resulted in a decrease in the content of that macroelement as well as a decrease in the activity of alkaline phosphatase both in the soil sampled in June and in October. The activity of acid phosphatase, due to increasing nitrogen rates, was increasing. Complete mineral fertilisation (P, K, Mg, S and Ca) fully satisfied the nutrition requirements of spring barley. There was identified a seasonal variation in the content of phosphorus and the activity of alkaline and acid phosphatase in the Luvisol.

Keywords: nitrogen, mineral fertilization, pH, available phosphorus, alkaline and acid phosphatases, soil

Including into the domestic law of the Regulation of Minister of Environment [DzU of 2003 No 4, item 44] [Regulation 2002] [1], pursuant to Nitrates Directive [Directive 91/676/EEC] [2], was the first step to reduce a negative effect on the environment. Thus there was recognised the effect of agroecosystems, especially the application of nitrogen and phosphorus, on the deterioration of the quality of waters, causing *eg* eutrophication. Unfortunately agricultural practise points to the fact that nitrogen fertilisation is preferred, as the basic yield-forming factor which, when provided in excessive amounts, results in soil and water contamination with nitrates. The supply of plants with nutrients

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in the adequate proportions is among the basic conditions of producing optimal crop yields [3, 4].

Chemicals uptaken from soil with yields are mostly supplemented by mineral fertilisation which, at the same time, modifies chemical and biochemical soil properties [5]. An excess of one of the minerals can cause or intensify the deficit of others, even when exposed to their optimum content in soil. This phenomenon is referred to as the antagonism of ions. A lack of balance between high rates of nitrogen, being the main yield-forming element, and the insufficient level of fertilisation with the other nutrients can lead to soil degradation and thus to a decrease in yields.

The aim of the paper was to determine the effect of fertilisation with increasing nitrogen rates and nutrients (P, K, Mg, Ca and S) on the content of available phosphorus and the activity of alkaline and acid phosphatase in soil under spring barley.

Material and methods

The present research was based on a many-year static field experiment, set up by the Department of Plant Nutrition and Fertilization of the *Institute of Soil Science and Plant Cultivation* (IUNG) in Pulawy. Strict experiments were performed in June and October 2008 in a long-term permanent experimental field located in the area of the Agricultural Experiment Station at Grabow on the Vistula, the Mazowieckie province, the zwolenski county, the commune of Przyleki. The location of the station is determined by latitude ($51^{o}21'8''$ N) and longitude ($21^{o}40'8''$ E). Lowland climate, of moderate latitudes. The soils the Agricultural Experiment Station at Grabow, represent Haplic Luvisols, of a very good rye complex soil. The experiment was performed in a four-year crop rotation: winter wheat + intercrop, corn for grain, spring barley, winter rape.

It was a two-factor experiment, in the randomised block design, in two reps. The first factor involved P, K, Mg, Ca and S fertilisation at six levels: 1 – (P, K, Mg, Ca and S), 2 – (K, Mg, Ca and S), 3 – (P, Mg, Ca and S), 4 – (P, K, Ca and S), 5 – (P, K, Mg, Ca), 6 – (P, K, Mg, S). The second factor involved nitrogen fertilisation at the following rates: 0, 30, 60, 90, 120, 150 $\mathrm{kgN \cdot ha^{-1}}$.

The following fertiliser forms were applied: for the treatments with S there were used phosphorus and potassium fertilisers containing sulphur: single superphosphate and potassium sulphate, for the treatment without sulphur there were used phosphorus and potassium fertilisers which do not include sulphur: triple superphosphate and high-percentage potassium salt, for the treatment with Ca and Mg there was applied dolomite containing 30 % CaO and 10 % Mg, in the plots without Mg, lime was used at the amount of 200 $\mathrm{kgCaO \cdot ha^{-1}}$, while in the case of Ca deficit, magnesium sulphate was supplied at the rate of 70 $\mathrm{kgMgO \cdot ha^{-1}}$. The rates of minerals applied in the experiment were as follows: 80 $\mathrm{kgP_2O_5 \cdot ha^{-1}}$, $\mathrm{140K_2O \cdot ha^{-1}}$, $\mathrm{70MgO \cdot ha^{-1}}$, $\mathrm{200CaO \cdot ha^{-1}}$. The S rate is a result of the sulphur amount introduced with adequate rates of P, K, Mg.

The soil was sampled twice: in June and in October 2008 under spring barley.

In the adequately prepared material, the following were determined:

– the content of available phosphorus ($P_{E\text{-}R}$) with the Egner-Riehm method – DL [6];

– the activity of alkaline (AlP) and acid (AcP) phosphatase with the Tabatabai, Bremner method [7];

– pH in H_2O [6].

The results were exposed to the analysis of variance and the significance of differences between means was verified with the Tukey test at the confidence level of p = 0.05. The calculations involved the use of FR-ANALWAR software based on Microsoft Excel. To identify the potential correlations between soil parameters the statistical analysis of the results was made applying the Statistica software.

Results and discussion

The mineral fertilisation applied in the experiment resulted in slight changes in the active soil acidity. The values of pH_{H_2O} ranged from 5.2 to 5.9 in soil depending on fertilisation (Table 1). Drawing on the pH_{H_2O} values recorded, the soil can be classified as acid.

Table 1

Exchangeable acidity of the Luvisol investigated, depending on differentiated increasing nitrogen rates and mineral fertilization (P, K, Mg, Ca, S)

Nitrogen [kg · ha^{-1}]	Mineral fertilization					
	P K Mg Ca S	K Mg Ca S	P Mg Ca S	P K Ca S	P K Mg S	P K Mg Ca
0	5.8	5.9	5.7	5.9	5.6	5.9
30	5.8	5.8	5.7	5.9	5.6	5.9
60	5.7	5.7	5.8	5.8	5.5	5.8
90	5.8	5.8	5.7	5.8	5.5	5.9
120	5.7	5.7	5.6	5.5	5.3	5.8
150	5.6	5.7	5.5	5.3	5.1	5.7

The content of available phosphorus in the Luvisol investigated was 57.74 mgP · kg^{-1}, which, according to the criteria provided for in PN-R-04023 [1996] [8], classifies it as class III, of an average content of P_{E-R}. Fotyma et al [9] claim that the optimal content of available phosphorus (determined with the Egner-Riehm method) should be 105–108 mgP · kg^{-1}. There was found a significant effect of a varied mineral fertilisation on the content of phosphorus in soil under spring barley. The highest content of that nutrient was reported in the soil sampled both in June (59.0 mgP · kg^{-1}) and in October (77.0 mgP · kg^{-1}) with complete mineral fertilisation (P, K, Mg, Ca, S) (Table 2). As a result of the lack of phosphorus fertilisation (K, Mg, Ca, S), a significant decrease in the content of P_{E-R} (by about 33 %) was noted, as compared with complete fertilisation. According to Szara et al [10], despite the lack of phosphorus fertilisation and persisting low content of available phosphorus in soil, the plants can uptake considerable amounts of phosphorus from the form which is hardly available. In the soil non-fertilised with Ca (P, K, Mg, S) there also occurred a decrease in P_{E-R} in the soil sampled in June (51.2 mgP · kg^{-1}) and in October (55.9 mgP · kg^{-1}) (Table 2). According to Bednarek and

Table 2

Content of available phosphorus [mgP · kg^{-1}] in the Luvisol investigated, depending on differentiated increasing nitrogen rates and mineral fertilization (P, K, Mg, Ca, S)

Mineral fertilization I factor	June							October						
	Nitrogen II factor [kgN · ha^{-1}]													
	0	30	60	90	120	150	Mean	0	30	60	90	120	150	Mean
P K Mg Ca S	76.5	67.0	61.0	58.1	50.5	41.1	59.0	87.8	92.6	81.2	73.8	69.8	56.8	77.0
K Mg Ca S	56.9	50.1	42.9	38.8	33.9	27.2	41.7	58.9	65.8	51.4	44.1	40.0	37.1	49.6
P Mg Ca S	64.7	59.9	55.8	51.1	46.1	39.1	52.8	79.9	88.0	73.2	66.1	57.5	49.6	69.1
P K Ca S	69.9	66.3	59.9	55.3	48.5	42.3	57.0	73.6	67.3	61.9	57.7	51.6	45.3	59.6
P K Mg S	61.2	58.3	52.8	49.9	46.1	39.1	51.2	66.9	69.9	58.7	57.3	43.1	40.0	55.9
P K Mg Ca	66.3	60.8	56.8	50.2	46.1	41.8	53.8	83.9	77.9	68.8	60.0	58.2	48.6	66.2
Mean	65.9	60.4	54.8	50.5	45.3	38.4	52.6	75.1	76.9	65.9	59.8	53.4	46.3	62.9
$LSD_{0.05}$														
I factor	1.178							1.456						
II factor	1.178							1.456						
Interaction														
I/II	2.885							3.567						
II/I	2.885							3.567						

Reszka [11], no liming increases the concentration of soluble and exchangeable ions of Fe and Al which can react with the phosphorus applied, which, as a result, leads to the formation of slightly soluble aluminium phosphates and iron phosphates. In the soil sampled from the treatments without sulphur (combination P, K, Mg, Ca), the content of available phosphorus in June was 53.8 mgP $\cdot$ kg^{-1}, while in October – 66.2 mgP $\cdot$ kg^{-1}. According to Kaczor and Laszcz-Zakorczmenna [4], sulphur deficit in soil can limit the uptake of basic nutrients by plants, including phosphorus, as a result of which the soil from the treatments non-fertilised with sulphur showed a greater richness with the available form of phosphorus.

Nitrogen fertilisation showed a significant effect on the content of available phosphorus in soil. In the soil sampled in June the highest content of the available form of phosphorus (65.9 mgP $\cdot$ kg^{-1}) was reported for the treatments non-fertilised with nitrogen, while in October the highest content of $P_{E\text{-}R}$ was recorded in the soil from the treatments fertilised with nitrogen at the rate of 30 kgN $\cdot$ ha^{-1} (76.9 mgP $\cdot$ kg^{-1}). Similarly Szymanska et al [12] claim that in the soil sampled from the treatments where for a few years nitrogen fertilisation had been applied, there was observed a decrease in the content of available phosphorus by an average of about 23 %, as compared with the soil from the treatments non-fertilised with nitrogen. The application of nitrogen at the rate of 150 kgN $\cdot$ ha^{-1} resulted in a clear decrease in the content of $P_{E\text{-}R}$ do 38.4 mgP $\cdot$ kg^{-1}. As the content of phosphorus critical for the plants 30 mgP $\cdot$ kg^{-1} soil is assumed. According to Rabikowska and Piszcz [13], many-year application of increasing nitrogen rates (maximum to 210 kgN $\cdot$ ha^{-1}) results in a decrease in soil fertility, an increase in its acidity, a decrease in the share of alkaline cations in the sorption capacity and in a decrease in the content of mobile forms of nutrients, including phosphorus. Most phosphorus is released when pH of soil ranges from 6 to 7.

The research demonstrated a significant effect of the fertilisation applied on the changes in the activity of alkaline and acid phosphatase in Luvisol. The highest AlP activity was noted in the soil sampled from the treatments without phosphorus fertilisation (K, Mg, Ca, S) (0.600 mM pNP/ kg $\cdot$ h in June, 0.777 mM pNP/kg $\cdot$ h in October) (Table 3). A high activity of that enzyme in soils points to an intensive rate of releasing anions $H_2PO_4^{-}$ and HPO_4^{2-} available to plants from organic bonds of phosphorus. For the plants it is an important source of supply with phosphorus, especially in the combinations non-fertilised with P-combination (K, Mg, Ca, S).

According to Heflik et al [14], Zebrowska et al [15], the reaction to phosphorus deficit in soil involves the production of phosphatases both via plant roots and microorganisms and so the activity of those enzymes is conditioned by the content of soil phosphorus, while Sapek [16] noted a lower efficiency of phosphorus mineralization once the fertilisation with that nutrient was abandoned, which could have been due to a poorer activity of soil microorganisms. As shown by Saggar et al [17], in the soils poorly fertilised with phosphorus the transformations of carbon are less intensive due to low efficiency of the microorganisms biomass.

The lowest activity of alkaline phosphatase (0.324 mM pNP/kg $\cdot$ h in June, 0.417 mM pNP/kg $\cdot$ h in October) was reported in the soil without liming (combination P, K,

Table 3

Activity of alkaline phosphatases [mM pNP/kg · h] in the Luvisol investigated, depending on differentiated increasing nitrogen rates and mineral fertilization (P, K, Mg, Ca, S)

Mineral fertilization I factor	June							October						
	Nitrogen II factor [kgN · ha^{-1}]													
	0	30	60	90	120	150	Mean	0	30	60	90	120	150	Mean
P K Mg Ca S	0.561	0.577	0.620	0.551	0.505	0.432	0.541	0.612	0.640	0.655	0.614	0.583	0.575	0.613
K Mg Ca S	0.596	0.610	0.659	0.630	0.572	0.533	0.600	0.789	0.814	0.832	0.770	0.747	0.710	0.777
P Mg Ca S	0.493	0.534	0.579	0.546	0.509	0.448	0.518	0.547	0.590	0.605	0.551	0.528	0.510	0.555
P K Ca S	0.330	0.392	0.441	0.383	0.358	0.288	0.365	0.452	0.481	0.498	0.445	0.420	0.403	0.450
P K Mg S	0.296	0.350	0.364	0.350	0.316	0.270	0.324	0.423	0.435	0.460	0.422	0.402	0.360	0.417
P K Mg Ca	0.455	0.478	0.507	0.494	0.454	0.416	0.467	0.560	0.586	0.593	0.540	0.509	0.502	0.548
Mean	0.455	0.490	0.528	0.492	0.452	0.398	0.469	0.564	0.591	0.607	0.557	0.531	0.510	0.560
LSD$_{0.05}$														
I factor				0.007							0.007			
II factor				0.007							0.007			
Interaction														
I/II				0.017							0.017			
II/I				0.017							0.017			

Mg, S). In those soils there was reported the lowest soil reaction (Table 1) which controls the activity of that enzyme considerably.

The fertilisation with nitrogen showed a significant effect on the activity of alkaline and acid phosphatase. Increasing nitrogen rates stimulated the activity of acid phosphatase, however, they inhibited the activity of alkaline phosphatase. After the nitrogen application at the rate of 150 kgN · ha^{-1} there was found the highest activity of acid phosphomonoesterase, while the activity of alkaline phosphatase was lowest, both in the soil sampled in summer and in autumn (Table 3). A poorer activity of alkaline phosphatase as a result of the increase in soil acidity is a result of the destruction of hydrogen and ionic bonds in the active enzyme centre so slight pH changes can decrease its activity. Excessively high nitrogen rates can lead to *eg* the accumulation of toxic substances or ammonia intoxicating plants and limiting the development of some groups of microorganisms being one of the sources of enzymes [18].

Based on the values of activity of alkaline and acid phosphatase recorded, there was calculated the ratio of AlP : AcP, referred to as the enzymatic index of the pH level [19]. The values of the AlP : AcP ratio throughout the research ranged from 0.28 to 0.57 (Fig. 1). The soil pH value to be considered adequate for the plant growth and development can be the one under the conditions of which there occurs the right ratio of the activity of AlP : AcP [19]. According to those authors [19], the value of the AlP : AcP ratio lower than 0.50 points to the acid reaction of soil and limiting is recommended. In the soil investigated for which no liming was applied (P, K, Mg, S), the value of the enzymatic index of the pH level was low (0.26–0.29). With the increasing nitrogen rate, the value of the AlP : AcP ratio in the soil decreased, after the application of the highest nitrogen rate (150 kgN · ha^{-1}) the AlP : AcP value was lowest (0.28–0.30). Similarly pH, measured in H_2O, was lowest in the soil fertilised with nitrogen at the rate of 150 kgN · ha^{-1}. Only in the soil sampled in June from the treatments fertilised with complete mineral fertilisation (combination P, K, Mg, Ca, S) and non-fertilised with nitrogen and at the rate of 30 kgN · ha^{-1}, the AlP : AcP value

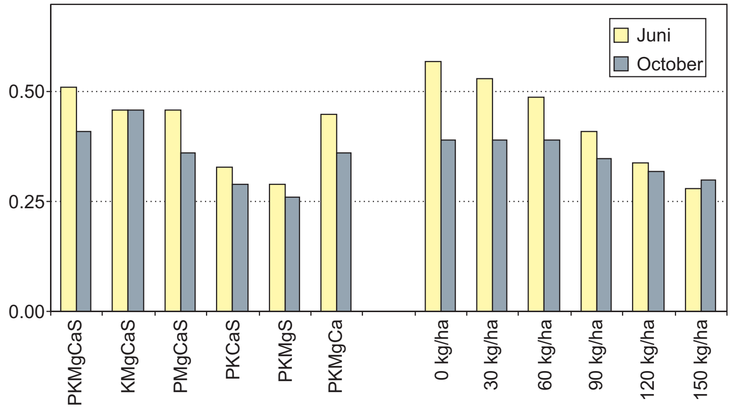

Fig. 1. Ratio of alkaline to acid phosphatase AlP : AcP in the Luvisol investigated, depending on the differentiated increasing nitrogen rates and mineral fertilization (P, K, Mg, Ca, S)

Table 4

Activity of acid phosphatases [mM pNP/kg · h] and the ratio of alkaline to acid phosphatase AlP : AcP in the Luvisol investigated, depending on differentiated increasing nitrogen rates and mineral fertilization (P, K, Mg, Ca, S)

Mineral fertilization I factor	June							October						
	Nitrogen II factor [kgN · ha^{-1}]													
	0	30	60	90	120	150	Mean	0	30	60	90	120	150	Mean
P K Mg Ca S	0.786	0.846	0.974	1.105	1.283	1.322	1.052	1.383	1.409	1.480	1.500	1.557	1.628	1.493
K Mg Ca S	0.973	1.140	1.224	1.388	1.504	1.598	1.304	1.593	1.627	1.664	1.726	1.781	1.807	1.699
P Mg Ca S	0.710	0.878	1.112	1.248	1.338	1.433	1.120	1.403	1.454	1.502	1.538	1.618	1.659	1.529
P K Ca S	0.798	0.882	1.037	1.197	1.289	1.361	1.094	1.443	1.490	1.539	1.595	1.593	1.688	1.558
P K Mg S	0.806	0.910	1.101	1.200	1.310	1.427	1.125	1.511	1.562	1.599	1.640	1.671	1.708	1.615
P K Mg Ca	0.752	0.847	0.977	1.065	1.192	1.366	1.033	1.407	1.457	1.496	1.560	1.616	1.685	1.537
Mean	0.804	0.917	1.071	1.200	1.319	1.417	1.121	1.457	1.499	1.547	1.593	1.639	1.696	1.572
LSD$_{0.05}$														
I factor				0.030							0.023			
II factor				0.030							0.023			
Interaction														
I/II				0.075							n.s.*			
II/I				0.075							n.s.*			

n.s.* – non-significant.

exceeded 0.5. The enzymatic index of the soil pH level can be used as an alternative method to determine the soil reaction and the transformations in it. A lack of organic or natural fertilisation resulted in the soil phosphorus depletion and soil acidification. FYM is a fertiliser alleviating the effects of unbalanced mineral fertilisation. In the soils demonstrating excessively high pH values, FYM can increase their acidity thanks to the formation of organic acids and carbon acid as a result of the hydrolysis and further mineralization of organic compounds.

A higher activity of both phosphatases (alkaline – 16 % higher, acid – 29 % higher) was found in the soil sampled in October, namely after spring barley harvest (Tables 3 and 4), which is connected with a long period of decomposition of organic matter in soil as post-harvest residue is a perfect source of energy for soil microorganisms.

The activity of acid phosphatase was closely connected with the content of phosphorus available to plants. The value of the coefficient of correlation between the activity of AcP and the content of $P_{E\text{-}R}$ in soil was $r = -0.97$, $p < 0.05$ (Table 5). The reports by Wyszolmirska et al [20] suggest that under available phosphorus deficit in the soil there occurs an increase in the activity of intercellular acid phosphatases in the plant tissues (cucumber, two oat cultivars). Similarly the surplus of available forms of phosphorus, which acts as a competition inhibitor, inhibits the synthesis of phosphatases. It is the phenomenon of enzyme repression and thus the inhibition of the activity of a given enzyme by an excess of the final product of the enzymatic activity. Bielinska and Ligeza [21], on the other hand, pointed to a strict correlation between the activity of phosphatases and the content of available phosphorus; a high activity of the phosphatases investigated was connected with the $P_{E\text{-}R}$. content, which was many-fold higher than in the soils of control treatments.

Table 5

Correlation coefficients between the enzymatic activity of soil and available phosphorus contents and pH

Parameters	Available phosphorus	pH
Alkaline phosphatase	n.s.	0.58*
Acid phosphatase	–0.97*	–0.59*

n.s. – non-significant.

There was reported a significant value of the coefficient of correlation between soil pH and the activity of alkaline phosphatase ($r = 0.58$, $p < 0.05$) (Table 5). Similarly Acosta-Martinez and Tabatabai [22] observed a high significant value of the coefficient of correlation ($r = 0.95^*$) for the pH and the alkaline phosphomonoesterase activity relationship. A significant, however, negative value of the coefficient of correlation ($r = -0.69$, $p < 0.05$) was reported by those authors for the activity of acid phosphatase and soil pH.

Conclusion

1. Considering the criteria provided for in PN-R-04023, the soil investigated demonstrated an average content of phosphorus available to plants. Nitrogen at the rate

over 30 kgN · h^{-1} resulted in a decrease in the content of available phosphorus in the soil, especially for the treatments non-fertilised with phosphorus.

2. The lack of balance between an insufficient level of fertilisation with P, K, Mg, Ca, S, and increasing nitrogen rates resulted in an unfavourable decrease in the content of phosphorus available in soil.

3. The increasing nitrogen rates resulted in an increase in the activity of acid phosphatase, while the activity of alkaline phosphatase was decreasing.

4. The values of the enzymatic index of the pH level call for soil liming, especially from the treatments fertilised with nitrogen at the rates over 30 kgN · h^{-1}.

5. The activity of alkaline and acid phosphatase was higher in the soil non-fertilised with phosphorus, which points to the participation of those enzymes in the biogeochemical phosphorus cycle.

6. The relationships between the content of available phosphorus in soil and the activity of alkaline and acid phosphatase demonstrate that they are mostly determined by the condition of the soil environment, affected mainly by intensive spring barley fertilisation.

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WPŁYW NAWOŻENIA AZOTEM JĘCZMIENIA JAREGO NA ZMIANY ZAWARTOŚCI FOSFORU I AKTYWNOŚCI FOSFATAZY ALKALICZNEJ I KWAŚNEJ W GLEBIE

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Abstrakt: Celem pracy było określenie zmian zawartości fosforu przyswajalnego i aktywności fosfatazy alkalicznej i kwaśnej pod wpływem nawożenia azotem w dawkach 0, 30, 60, 90, 120, 150 kgN · ha^{-1} oraz nawożenia mineralnego (P, K, Mg, Ca i S) w glebie spod uprawy jęczmienia jarego. Próbki glebowe pobrano w czerwcu i w październiku 2008 r. z doświadczenia polowego założonego na terenie RZD w Grabowie nad Wisłą, przez IUNG w Puławach. Stwierdzono istotny wpływ nawożenia azotem na zawartość fosforu przyswajalnego w badanej glebie. Duże dawki azotu powodowały zmniejszenie zawartości tego makroskładnika, jak również obniżenie aktywności fosfatazy alkalicznej zarówno w glebie pobranej w czerwcu, jak i październiku. Aktywność fosfatazy kwaśnej pod wpływem wzrastających dawek azotu zwiększała się. Pełne nawożenie mineralne (P, K, Mg, S i Ca) w pełni zaspokoiło potrzeby pokarmowe jęczmienia jarego. Stwierdzono sezonowe zróżnicowanie zawartości fosforu oraz aktywności fosfatazy alkalicznej i kwaśnej w badanej glebie płowej.

Słowa kluczowe: azot, nawożenie mineralne, pH, fosfor przyswajalny, fosfataza alkaliczna i kwaśna, gleba

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WATER CHEMISTRY OF SELECTED SOUTH PODLASIE LOWLAND RIVERS

CHEMIZM WODY WYBRANYCH RZEK NIZINY POŁUDNIOWOPODLASKIEJ

Abstract: In this paper results of the water quality investigations were presented. Samples of water were taken from four rivers in middle-eastern Poland: Kostrzyn, Mienia, Osownica and Wilga. Quarterly investigations covered analysis of water reaction, electrical conductivity, dissolved oxygen and biochemical oxygen demand, total concentration of twenty six elements by inductively coupled plasma atomic emission spectrometry (ICP-AES). The resulting data were processed statistically using arithmetic means, concentration ranges, standard deviations and relative standard deviations. Due to the effect of sample collection date on concentrations of analyzed elements, a single factor analysis of variance and Tukey post-hoc test were completed. It was found that the quality of water in the rivers was differential if selected water quality indicators were taken account. The values of this indicators were dependent on location of checkpoints, season and type of surrounding grounds cultivation. The quality of water in particular checkpoints was affected by anthropogenic sources of contamination: community waste from private possessions and sewage from fertilized arable land and greenlands.

Keywords: surface water quality, water quality indicators, sources of contamination, ICP-AES

Purity of surface and underground waters is very important from both an ecological and economic point of view. The decreasing extent of the use of surface water is a consequence of the quality of those waters which does not meet the standards set for water intended for consumption and for use in individual branches of the economy. The main factors which directly affect the diversity of chemical composition of surface waters are: geochemical properties of the drainage basin [1] and the amount of rainfall and methods of use of adjacent land [2–5]. The load of anthropogenic contamination introduced directly or as contaminated rainfall, can greatly affect the water quality. The chemical composition of the water also depends on seasonal changes of flow intensity, temperature, climate humidity and biological activity [6]. Water resources are frequently

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degraded by industrial, communal and agricultural pollutants being discharged to them [7, 8]. The ability of flowing water to regenerate varies and depends mainly on the presence and effect of anthropogenic factors. The knowledge of changes in soluble substance concentration helps to evaluate the natural chemical composition and the effect of human economic activities on the quality of surface waters.

The aim of the study was to evaluate the purity of the Kostrzyn, the Mienia, the Osownica and the Wilga rivers based on selected indicators of surface water quality as well as an interpretation of the spatial and seasonal changes in the water quality.

Materials and methods

Samples taken from the Kostrzyn (7 sampling sites), the Osownica (7), the Mienia (11) and the Wilga (10) rivers in the central-eastern part of Poland were used in the study. Water samples for analysis were taken seasonally at intervals of a quarter of a year in the years 2005/2006. The following were determined immediately after sampling: pH – by the potentiometric method with the use of a combined electrode and a 301 pH-meter, manufactured by Hanna Instruments; electrolytic conductivity – by the electrochemical method with an HI 2300 conductometer, manufactured by Hanna Instruments; concentration of dissolved oxygen – electrochemically with the use of an HI 9143 dissolved oxygen probe, manufactured by Hanna Instruments. The BOD_5 value was calculated from the results of determination of dissolved oxygen *in situ* and after a five-day period of incubation with an oxygen probe, without diluting the samples. Subsequently, 5 cm^3 of concentrated HNO_3 was added to 45 cm^3 of water and mineralised in a Multiwave microwave sample preparation system, manufactured by Anton Paar. The total content of 26 elements (P, K, Ca, Mg, Na, S, Fe, Al, Mn, Co, Mo, B, Li, Ti, Ba, Sr, V, Se, Sn, As, Pb, Cd, Cr, Cu, Zn, Ni) was determined by the ICP-AES method on an Optima 3200RL spectrometer, manufactured by Perkin Elmer. The method enabled simultaneous determination of the concentration of many elements at low levels of detectability and a relatively low effect of the sample matrix [9]. The results were worked out statistically by calculating arithmetic averages, concentration ranges, *standard deviations* (SD) and *relative standard deviation* (RSD) and performing a single-factor analysis of variance and Tukey's test at the levels of significance $\alpha = 0.05$ and $\alpha = 0.01$.

Results and discussion

The values of selected physical indexes of salinity and quality of waters corresponded generally to class I and II of surface water quality (Tables 1–4). The values corresponding to classes III, IV and V were recorded in the case of Fe, Mn and Al, but not for P and Cr. Elevated values of Cr content were found in the Wilga in spring and in the Kostrzyn in winter. This was probably a consequence of discharging communal wastewater. In the Kostrzyn, spot distribution of the pollution was observed and self-purification of the water took place down the river. The concentrations of Co, Mo, V, Se, Sn, As, Pb and Cd lay within the detection limits of the method and were equal to

Table 1

Statistical assessment of selected water quality indicators and analyzed elements contents in Kostrzyn River

Indicator	Spring					Summer					Autumn					Winter				
	mean	min	max	SD	RSD	mean	min	max	SD	RSD	mean	min	max	SD	RSD	mean	min	max	SD	RSD
pH	7.36	7.05	7.67	0.22	3	7.26	6.95	7.52	0.24	3	7.34	7.06	7.69	0.24	3	7.24	7.03	7.46	0.16	2
EC [$\mu S \cdot cm^{-1}$]	413	381	507	44	11	397	346	447	30	8	384	327	419	28	7	385	325	422	30	8
O_2 [$mg \cdot dm^{-3}$]	8.82	7.90	9.72	0.66	7	6.34	6.00	6.74	0.28	4	8.40	7.93	8.88	0.35	4	10.20	8.43	11.60	0.97	10
BOD_5 [$mg \cdot dm^{-3}$]	1.27	0.46	3.36	0.99	78	2.40	1.88	2.92	0.41	17	2.43	2.10	2.97	0.34	14	2.96	2.10	4.41	0.92	31
P [$mg \cdot dm^{-3}$]	0.124	0.098	0.176	0.026	21	0.285	0.232	0.461	0.084	29	0.142	0.117	0.164	0.016	11	0.061	0.008	0.088	0.027	45
K [$mg \cdot dm^{-3}$]	2.19	1.89	2.41	0.20	9	2.17	1.67	2.97	0.40	18	2.28	2.17	2.46	0.12	5	1.61	1.46	1.89	0.13	8
Ca [$mg \cdot dm^{-3}$]	55.6	51.2	60.4	3.5	6	68.4	65.7	74.6	3.1	5	61.9	59.6	64.0	1.4	2	59.5	56.4	62.0	2.0	3
Mg [$mg \cdot dm^{-3}$]	5.18	4.47	5.62	0.46	9	6.93	6.01	7.90	0.62	9	6.51	6.15	6.90	0.25	4	5.35	4.76	6.03	0.44	8
Na [$mg \cdot dm^{-3}$]	12.39	11.40	13.45	0.72	6	7.17	5.65	7.90	0.72	10	6.98	6.34	7.44	0.41	6	5.64	5.17	6.14	0.34	6
S [$mg \cdot dm^{-3}$]	12.79	11.81	13.61	0.67	5	10.91	9.41	13.70	1.42	13	5.43	3.75	6.91	1.04	19	11.50	9.99	13.88	1.36	12
Fe [$mg \cdot dm^{-3}$]	0.676	0.593	0.852	0.091	13	1.580	1.090	3.185	0.762	48	1.134	0.842	1.467	0.214	19	0.486	0.025	0.690	0.216	44
Al [$mg \cdot dm^{-3}$]	0.113	0.089	0.158	0.023	21	0.110	0.035	0.442	0.148	135	0.142	0.076	0.225	0.061	43	0.072	0.000	0.116	0.039	55
Mn [$mg \cdot dm^{-3}$]	0.135	0.109	0.183	0.027	20	0.220	0.122	0.424	0.098	45	0.140	0.118	0.161	0.015	10	0.130	0.053	0.179	0.041	31
B [$mg \cdot dm^{-3}$]	0.024	0.015	0.043	0.010	43	0.011	0.002	0.021	0.006	54	0.059	0.035	0.089	0.018	30	0.008	0.002	0.021	0.007	88
Li [$mg \cdot dm^{-3}$]	0.002	0.001	0.002	0.000	21	0.001	0.001	0.002	0.000	32	0.005	0.004	0.006	0.001	14	0.001	0.000	0.001	0.000	60
Ti [$mg \cdot dm^{-3}$]	0.000	0.000	0.000	0.000	188	0.001	0.000	0.009	0.003	248	0.002	0.000	0.005	0.002	66	0.001	0.000	0.004	0.001	97
Ba [$mg \cdot dm^{-3}$]	0.048	0.043	0.055	0.004	9	0.058	0.050	0.071	0.008	13	0.035	0.029	0.048	0.006	18	0.039	0.028	0.048	0.008	20
Sr [$mg \cdot dm^{-3}$]	0.121	0.103	0.141	0.017	14	0.184	0.168	0.202	0.011	6	0.127	0.125	0.132	0.002	2	0.111	0.097	0.124	0.010	9
Cr [$mg \cdot dm^{-3}$]	0.003	0.001	0.006	0.002	50	0.005	0.000	0.014	0.005	105	0.003	0.001	0.005	0.001	39	0.178	0.000	1.239	0.468	262
Cu [$mg \cdot dm^{-3}$]	0.008	0.007	0.009	0.000	4	< 0.004*					0.004	0.000	0.007	0.002	59	0.009	0.004	0.022	0.006	71
Zn [$mg \cdot dm^{-3}$]	0.066	0.049	0.091	0.018	27	0.016	0.000	0.035	0.012	77	0.004	0.000	0.011	0.005	116	0.064	0.000	0.123	0.045	70
Ni [$mg \cdot dm^{-3}$]	< 0.002*					0.034	0.000	0.228	0.086	251	< 0.002*									

* Content below the detection limit of the analytical method.

Table 2

Statistical assessment of selected water quality indicators and analyzed elements contents in Mienia River

Indicator	Spring					Summer					Autumn					Winter				
	mean	min	max	SD	RSD	mean	min	max	SD	RSD	mean	min	max	SD	RSD	mean	min	max	SD	RSD
pH	7.65	7.40	7.80	0.13	2	7.68	7.30	8.40	0.41	5	7.60	7.40	7.70	0.10	1	7.62	7.50	7.70	0.09	1
EC [$\mu S \cdot cm^{-1}$]	520	474	601	46	9	587	447	936	139	24	620	539	760	58	9	673	564	759	62	9
O_2 [$mg \cdot dm^{-3}$]	10.30	9.63	11.20	0.47	5	7.26	3.82	11.80	2.69	37	9.55	5.82	12.30	1.69	18	10.31	8.15	11.10	0.87	8
BOD_5 [$mg \cdot dm^{-3}$]	3.28	2.16	4.56	0.78	24	3.67	2.20	6.56	1.11	30	5.42	3.04	6.99	1.26	23	2.38	1.78	3.20	0.49	21
P [$mg \cdot dm^{-3}$]	0.275	0.111	0.501	0.144	52	0.969	0.198	4.625	1.242	128	0.534	0.073	1.946	0.575	108	0.319	0.023	0.667	0.266	83
K [$mg \cdot dm^{-3}$]	4.78	3.86	6.46	0.92	19	6.21	3.54	14.50	3.18	51	6.36	2.13	12.65	3.67	58	5.08	2.60	8.06	2.44	48
Ca [$mg \cdot dm^{-3}$]	62.7	57.0	66.1	3.1	5	83.3	66.2	114.0	15.7	19	83.7	68.0	102.5	12.9	15	83.3	67.9	106.2	11.7	14
Mg [$mg \cdot dm^{-3}$]	8.48	7.66	9.07	0.47	6	11.24	8.51	14.85	2.45	22	11.85	9.61	15.01	1.84	16	10.53	8.99	12.84	1.28	12
Na [$mg \cdot dm^{-3}$]	33.92	17.01	57.32	16.54	49	18.35	9.07	54.00	13.21	72	22.78	9.20	46.72	13.92	61	28.17	11.34	49.90	17.14	61
S [$mg \cdot dm^{-3}$]	13.86	10.85	16.45	2.15	16	13.58	8.52	19.55	2.94	22	19.36	14.39	28.08	3.82	20	18.60	14.80	22.01	2.51	13
Fe [$mg \cdot dm^{-3}$]	0.640	0.239	1.111	0.266	42	1.454	0.583	4.110	1.227	84	1.102	0.269	5.108	1.478	134	0.608	0.332	1.125	0.221	36
Al [$mg \cdot dm^{-3}$]	0.099	0.009	0.234	0.062	63	0.390	0.040	2.465	0.697	179	0.179	0.000	1.205	0.368	206	0.126	0.049	0.361	0.088	70
Mn [$mg \cdot dm^{-3}$]	0.145	0.062	0.224	0.051	35	0.745	0.122	3.050	1.108	149	0.221	0.052	1.094	0.298	135	0.155	0.089	0.263	0.044	28
B [$mg \cdot dm^{-3}$]	0.041	0.013	0.090	0.024	60	0.051	0.012	0.162	0.046	90	0.088	0.016	0.181	0.061	69	0.039	0.009	0.088	0.029	72
Li [$mg \cdot dm^{-3}$]	0.002	0.000	0.002	0.001	34	0.004	0.002	0.007	0.002	50	0.007	0.005	0.008	0.001	17	0.002	0.001	0.003	0.001	28
Ti [$mg \cdot dm^{-3}$]	0.004	0.001	0.011	0.003	78	0.006	0.000	0.046	0.013	223	0.002	0.000	0.017	0.005	228	0.001	0.000	0.005	0.002	141
Ba [$mg \cdot dm^{-3}$]	0.050	0.043	0.057	0.003	7	0.061	0.045	0.113	0.020	33	0.043	0.026	0.095	0.020	48	0.066	0.050	0.137	0.025	37
Sr [$mg \cdot dm^{-3}$]	0.188	0.162	0.211	0.018	10	0.173	0.143	0.207	0.020	12	0.152	0.123	0.179	0.017	11	0.137	0.103	0.159	0.019	14
Cr [$mg \cdot dm^{-3}$]	0.004	0.001	0.016	0.004	103	0.002	0.000	0.013	0.004	176	0.005	0.001	0.013	0.004	85	0.001	0.000	0.002	0.001	107
Cu [$mg \cdot dm^{-3}$]	0.000	0.000	0.005	0.001	332	< 0.004*					0.001	0.000	0.005	0.002	217	0.001	0.000	0.002	0.001	143
Zn [$mg \cdot dm^{-3}$]	0.001	0.000	0.015	0.005	308	0.019	0.001	0.045	0.015	80	0.002	0.000	0.010	0.004	222	0.006	0.000	0.030	0.009	142
Ni [$mg \cdot dm^{-3}$]	0.004	0.000	0.009	0.004	89	0.024	0.000	0.191	0.056	232	0.007	0.000	0.021	0.006	90	0.002	0.000	0.011	0.004	174

* Content below the detection limit of the analytical method.

Table 3

Statistical assessment of selected water quality indicators and analyzed elements contents in Osownica River

Indicator	Spring					Summer					Autumn					Winter				
	mean	min	max	SD	RSD	mean	min	max	SD	RSD	mean	min	max	SD	RSD	mean	min	max	SD	RSD
pH	7.44	7.25	7.98	0.25	3	7.39	7.20	7.69	0.16	2	7.42	7.35	7.54	0.07	1	7.56	7.23	7.87	0.19	3
EC [$\mu S \cdot cm^{-1}$]	379	322	420	31	8	465	432	487	18	4	432	412	452	14	3	421	347	457	36	9
O_2 [$mg \cdot dm^{-3}$]	9.07	8.68	9.36	0.23	3	5.87	5.61	6.15	0.20	3	7.51	7.04	8.12	0.42	6	10.12	8.94	11.46	0.79	8
BOD_5 [$mg \cdot dm^{-3}$]	1.69	0.71	2.94	0.82	48	1.55	0.86	2.48	0.69	44	2.89	2.50	3.23	0.29	10	2.38	1.69	3.39	0.60	25
P [$mg \cdot dm^{-3}$]	0.127	0.098	0.159	0.024	19	0.289	0.219	0.558	0.122	42	0.091	0.058	0.162	0.042	46	0.093	0.052	0.147	0.032	34
K [$mg \cdot dm^{-3}$]	2.97	2.65	3.21	0.22	7	2.76	2.28	3.22	0.33	12	2.47	2.17	2.75	0.22	9	2.13	1.91	2.52	0.20	10
Ca [$mg \cdot dm^{-3}$]	50.7	46.8	54.1	2.3	4	76.3	69.9	85.0	5.6	7	71.2	68.7	75.5	2.3	3	68.4	64.3	73.6	3.2	5
Mg [$mg \cdot dm^{-3}$]	6.23	5.75	6.52	0.28	5	11.35	10.07	12.95	1.14	10	9.81	8.64	11.22	0.86	9	8.38	7.64	9.89	0.79	9
Na [$mg \cdot dm^{-3}$]	12.30	10.78	13.31	0.91	7	6.17	5.05	9.06	1.41	23	5.15	4.88	5.51	0.20	4	5.79	5.09	6.88	0.56	10
S [$mg \cdot dm^{-3}$]	10.65	9.64	11.72	0.68	6	11.01	8.79	13.35	1.70	15	6.79	6.36	7.31	0.38	6	9.62	9.12	10.54	0.45	5
Fe [$mg \cdot dm^{-3}$]	0.670	0.552	0.971	0.145	22	2.251	1.335	5.320	1.367	61	0.898	0.533	1.549	0.462	51	0.950	0.534	1.491	0.332	35
Al [$mg \cdot dm^{-3}$]	0.172	0.131	0.234	0.034	20	0.352	0.188	0.819	0.216	61	0.075	0.000	0.345	0.130	173	0.121	0.062	0.172	0.042	35
Mn [$mg \cdot dm^{-3}$]	0.194	0.087	0.275	0.071	37	0.401	0.232	1.145	0.330	82	0.140	0.110	0.216	0.042	30	0.173	0.143	0.190	0.020	12
B [$mg \cdot dm^{-3}$]	0.036	0.020	0.050	0.014	40	0.012	0.002	0.029	0.010	77	0.035	0.016	0.081	0.024	69	0.015	0.001	0.050	0.022	144
Li [$mg \cdot dm^{-3}$]	0.003	0.003	0.003	0.000	5	0.005	0.004	0.006	0.001	13	0.006	0.006	0.007	0.001	9	0.002	0.002	0.003	0.001	22
Ti [$mg \cdot dm^{-3}$]	0.001	0.000	0.004	0.001	106	0.004	0.001	0.013	0.004	94	0.001	0.000	0.008	0.003	212	0.003	0.000	0.007	0.003	107
Ba [$mg \cdot dm^{-3}$]	0.058	0.051	0.072	0.007	12	0.093	0.075	0.128	0.018	19	0.051	0.040	0.061	0.009	18	0.065	0.057	0.077	0.008	12
Sr [$mg \cdot dm^{-3}$]	0.138	0.118	0.156	0.015	11	0.290	0.248	0.328	0.031	11	0.205	0.160	0.247	0.031	15	0.171	0.144	0.218	0.027	16
Cr [$mg \cdot dm^{-3}$]	0.005	0.002	0.015	0.005	98	0.011	0.003	0.024	0.009	79	0.003	0.001	0.005	0.002	47	0.000	0.000	0.001	0.000	256
Cu [$mg \cdot dm^{-3}$]	0.009	0.008	0.012	0.001	17	< 0.004*														
Zn [$mg \cdot dm^{-3}$]	0.071	0.037	0.104	0.024	34	0.034	0.015	0.069	0.020	60	0.006	0.000	0.017	0.007	127	0.015	0.000	0.056	0.021	136
Ni [$mg \cdot dm^{-3}$]	< 0.002*																			

* Content below the detection limit of the analytical method.

Table 4

Statistical assessment of selected water quality indicators and analyzed elements contents in Wilga River

Indicator	Spring					Summer					Autumn					Winter				
	mean	min	max	SD	RSD	mean	min	max	SD	RSD	mean	min	max	SD	RSD	mean	min	max	SD	RSD
pH	7.29	7.00	7.56	0.17	2	7.72	7.55	7.89	0.11	1	8.08	7.73	8.36	0.23	3	7.69	7.47	7.91	0.13	2
EC [$\mu S \cdot cm^{-1}$]	381	300	640	81	21	584	393	1185	197	34	528	499	591	28	5	536	433	628	53	10
O_2 [$mg \cdot dm^{-3}$]	10.74	9.61	12.25	0.58	5	9.54	7.03	10.90	0.97	10	10.22	9.40	11.15	0.59	6	10.75	9.78	11.20	0.39	4
BOD_5 [$mg \cdot dm^{-3}$]	5.19	4.38	6.55	0.67	13	5.40	3.16	10.01	2.45	45	4.27	3.53	5.02	0.50	12	6.09	2.89	10.27	2.36	39
P [$mg \cdot dm^{-3}$]	0.135	0.091	0.199	0.038	28	0.078	0.000	0.213	0.088	113	0.247	0.076	0.634	0.189	76	0.213	0.148	0.314	0.054	26
K [$mg \cdot dm^{-3}$]	3.50	2.42	6.56	1.69	48	4.03	3.08	5.38	1.00	25	3.48	2.79	4.81	0.86	25	3.40	3.19	3.83	0.22	7
Ca [$mg \cdot dm^{-3}$]	73.6	68.0	76.1	2.8	4	72.3	48.5	82.6	12.8	18	76.9	73.1	83.0	3.8	5	49.6	39.3	54.0	4.8	10
Mg [$mg \cdot dm^{-3}$]	9.20	8.62	9.56	0.37	4	9.81	9.54	10.33	0.30	3	9.09	8.37	9.85	0.48	5	5.45	4.41	5.90	0.53	10
Na [$mg \cdot dm^{-3}$]	14.42	7.69	34.52	11.51	80	14.99	9.13	28.34	8.68	58	16.16	9.70	29.32	8.49	53	5.71	4.34	7.83	1.38	24
S [$mg \cdot dm^{-3}$]	10.93	8.02	15.76	2.89	26	10.78	9.36	13.02	1.52	14	12.85	12.00	14.57	0.92	7	13.29	11.75	13.87	0.78	6
Fe [$mg \cdot dm^{-3}$]	1.154	0.504	2.705	0.741	64	0.330	0.185	0.567	0.162	49	1.466	0.941	2.317	0.553	38	0.632	0.417	0.971	0.226	36
Al [$mg \cdot dm^{-3}$]	< 0.05*					0.045	0.010	0.119	0.044	96	0.090	0.031	0.156	0.049	55	0.070	0.008	0.167	0.060	86
Mn [$mg \cdot dm^{-3}$]	0.228	0.153	0.296	0.047	20	0.099	0.041	0.193	0.059	59	0.336	0.253	0.416	0.059	18	0.131	0.093	0.162	0.027	20
B [$mg \cdot dm^{-3}$]	0.008	0.000	0.020	0.007	85	0.027	0.010	0.051	0.016	59	0.036	0.010	0.115	0.036	99	0.007	0.000	0.019	0.009	116
Li [$mg \cdot dm^{-3}$]	0.003	0.002	0.004	0.001	20	0.003	0.002	0.003	0.000	11	0.002	0.002	0.003	0.000	21	< 0.001*				
Ti [$mg \cdot dm^{-3}$]	0.001	0.000	0.005	0.002	170	0.001	0.000	0.004	0.002	228	0.001	0.000	0.004	0.002	125	0.003	0.000	0.007	0.003	91
Ba [$mg \cdot dm^{-3}$]	0.064	0.060	0.067	0.003	4	0.057	0.046	0.067	0.008	14	0.075	0.061	0.088	0.010	13	0.003	0.000	0.009	0.003	95
Sr [$mg \cdot dm^{-3}$]	0.275	0.239	0.327	0.029	11	0.234	0.215	0.279	0.024	10	0.228	0.197	0.263	0.021	9	0.095	0.078	0.108	0.012	13
Cr [$mg \cdot dm^{-3}$]	0.129	0.020	0.441	0.143	111	< 0.001*														
Cu [$mg \cdot dm^{-3}$]	< 0.004*					0.005	0.000	0.024	0.009	164	< 0.004*									
Zn [$mg \cdot dm^{-3}$]	0.025	0.005	0.054	0.017	68	0.002	0.000	0.009	0.004	173	0.018	0.000	0.079	0.031	173	0.050	0.012	0.101	0.037	75
Ni [$mg \cdot dm^{-3}$]	0.064	0.011	0.215	0.069	107	< 0.002*														

* Content below the detection limit of the analytical method.

0.001, 0.001, 0.001, 0.05, 0.004, 0.02, 0.008, 0.0009 mg · cm^{-3}, respectively. These elements are not shown in the Tables.

A single-factor analysis of variance showed the highly significant ($\alpha = 0.01$) effect of the date of sampling on the content of Ca (20 % of explained variance), Mg (21 %), Fe (11 %), B (17 %), Li (41 %), Ba (12 %), Sr (30 %) and Zn (18 %) and the significant effect ($\alpha = 0.05$) of the concentration of Mn (7 %). The results indicate a higher effect of the sampling site on the variance of concentration of the analysed elements than the sampling date. Higher average concentrations of each element were found in summer and autumn, which can be attributed to the diminiution of the river waters caused by the decreasing seasonal water levels (Table 5).

Table 5

Mean contents of analyzed elements and homogeneous groups of means

Sample collection date	Mean	Homogeneous groups of means		Sample collection date	Mean	Homogeneous groups of means		
Ca [mg · dm^{-3}]				Fe [mg · dm^{-3}]				
Spring	61.9	*		Winter	0.643	*		
Summer	65.9	*		Spring	0.803	*	*	
Autumn	75.0		*	Autumn	1.16		*	*
Winter	76.1		*	Summer	1.33			*
Mg [mg · dm^{-3}]				Li [mg · dm^{-3}]				
Spring	7.52	*		Winter	0.001	*		
Winter	7.58	*		Spring	0.002	*	*	
Autumn	9.54		*	Summer	0.003		*	
Summer	9.92		*	Autumn	0.005			*
B [mg · dm^{-3}]				Sr [mg · dm^{-3}]				
Winter	0.019	*		Winter	0.125	*		
Spring	0.027	*		Autumn	0.174		*	
Summer	0.030	*		Spring	0.183		*	*
Autumn	0.057		*	Summer	0.211			*
Ba [mg · dm^{-3}]				Zn [mg · dm^{-3}]				
Winter	0.044	*		Autumn	0.006	*		
Autumn	0.052	*		Summer	0.017	*	*	
Spring	0.055	*	*	Winter	0.031		*	*
Summer	0.065		*	Spring	0.039			*
Mn [mg · dm^{-3}]								
Winter	0.145	*						
Spring	0.172	*	*					
Autumn	0.213	*	*					
Summer	0.388		*					

In the case of Zn, this was observed in spring and in winter, which was probably caused by introducing anthropogenic pollutants, especially by discharging industrial, communal and agricultural sewage.

Conclusions

1. The water quality in the Kostrzyn, Mienia, Osownica and Wilga rivers varied in terms of the quality indicators under study. The values of selected indicators were affected by the location of the sampling site (geochemical properties of the drainage basin and the method of use of adjacent terrain) and, to a lesser extent, the sampling date (seasonal changes of the flow intensity, temperature, climate humidity and biological activity). The differences in concentrations of the indicators in water between different sampling sites are a consequence of pollution and the natural self-purification of water.

2. The overall concentration of the elements in the water of the rivers under study can be arranged in decreasing order:

– macroelements:
  Ca > S > Na > Mg > K > P (in the Kostrzyn);
  Ca > Na > S > Mg > K > P (in the Mienia and the Wilga);
  Ca > S > Mg > Na > K > P (in the Osownica);
– selected microelements and trace elements:
  Fe > Mn > Al > Sr > Ba > B > Li > Ti (in the Mienia);
  Fe > Mn > Sr > Al > Ba > B > Li > Ti (in the Kostrzyn, the Osownica and the Wilga).

3. The content of heavy metals in the rivers was low. The Pb and Cd content was lower than the detection limit of the method applied, therefore, the rivers can be included in class I and II of surface water quality. Elevated concentrations of the other metals were recorded sporadically, at sites affected by spot pollution sources.

4. An analysis of the chemical composition and selected indicators of water quality of the rivers under study indicates only a low degree of hazard to the aquatic environment. However, efforts should be made to minimize the effect that anthropogenic sources of pollution have on water quality, *eg* run-off from fertilized agricultural land, inflow of communal waste and uncontrolled discharge of industrial and agricultural waste.

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CHEMIZM WODY WYBRANYCH RZEK NIZINY POŁUDNIOWOPODLASKIEJ

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Abstrakt: W pracy przedstawiono wyniki badań jakości wód rzek w środkowo-wschodniej części Polski: Kostrzynia, Mieni, Osownicy i Wilgi. Próbki wody pobierano sezonowo w odstępach kwartalnych. Badano w nich odczyn, przewodnictwo właściwe, stężenie tlenu rozpuszczonego w wodzie i BZT_5 oraz zawartość 26 pierwiastków metodą ICP-AES. Uzyskane dane opracowano statystycznie podając średnie arytmetyczne, zakresy stężeń, odchylenie standardowe (SD) oraz względne odchylenie standardowe (RSD). Z uwagi na wpływ terminu pobrania próbki na zawartość pierwiastków przeprowadzono jednoczynnikową analizę wariancji. Stwierdzono, że jakość wód analizowanych rzek była zróżnicowana w zakresie badanych wskaźników jakości. Na wartość wybranych wskaźników wpływała głównie lokalizacja pobrania próbki wody, pora roku oraz sposób użytkowania terenów przyległych. Zróżnicowaną jakość pobieranej wody powodowały antropogenne źródła zanieczyszczeń, a przede wszystkim zrzuty ścieków komunalnych z prywatnych posesji i spływy z nawożonych terenów rolniczych. Sporadyczne występowanie podwyższonych wartości niektórych wskaźników miało charakter punktowy i zmniejszało się w dalszym biegu rzek.

Słowa kluczowe: jakość wód powierzchniowych, wskaźniki jakości, źródła zanieczyszczeń, ICP-AES

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AFFECT OF AGRICULTURAL SYSTEMS ON BIODIVERSITY

ODDZIAŁYWANIE SYSTEMÓW ROLNICZYCH NA BIORÓŻNORODNOŚĆ

Abstract: Biodiversity is understood as "diversifying of all living organisms existing on Earth in continental ecosystems, marine and freshwater, and in environmental groups, which are the part of them". This includes diversity within species, between species, and ecosystem diversity. According to many authors, biodiversity in the agricultural landscape and agroecosystems plays greater role than natural ecosystems. Disappearance of sensitive organisms is due to direct changes in biocenoses structure and indirect impact of humans on organisms trough affecting soil conditions, the quality of water and air. For the protection of biological diversity preventing species extinction in the wild state is a priority task. Over the past hundred years many wild species of plants have disappeared as well as their unique genotypes. Most of the genous stores of plants is within the populations of crop species assessed in terms of genetic diversity on the basis of the number of registered varieties. For example, the register of varieties of agricultural crops from the year 2008 shows more than 1100 varieties of plant crops, large part of which comes from outside of our country. In addition to this day, the fragmented and extensive agricultural economy has survived many local or old varieties of cereals, vegetables, fodder plants and fruit trees, among which there are also varieties with relict character (false flax, oily variety of common reddish, true millet).

Keywords: biodiversity, nature, cereals, weeds, meadow

Nowadays about 10 million species live on Earth, and perhaps many more existing species even do not have a name. This shows the multitude and variety of forms, which can be revitalized. There are many different definitions of biodiversity; however, the one which is the most commonly used, was proposed in the text of the Convention on Biological Diversity from the "Earth Top" in Rio de Janeiro from 5 June 1992. According to this concept biodiversity is "diversifying of all living organisms existing on Earth in continental ecosystems, marine and freshwater, and in environmental

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groups, which are the part of them”. This includes diversity within species, between species and ecosystem diversity.

If you measure the biodiversity with a degree of conservation of species or communities originally found in Poland and forms of plants [1] as well as breeds of animals. our country can be considered as an area of a relatively high biodiversity. Highly endangered species in other countries, especially in Western Europe, are quite numerous animals (white stork, corncrake, beaver, otter) and plants (lung worth, forestry holy grass, cockle grasshopper). Many species of plants and animals in the area of Poland are on the edge of extinction [2]. It is due to the fragmentation of farming in Poland what reached many local varieties of plants and breeds of livestock.

Nevertheless, a significant part of our flora is threatened with extinction, and a red list of species has been getting longer almost from year to year [3].

Antropopresive and biodiversity

According to many authors [4, 5] biodiversity in the agricultural landscape. and agroecosystems plays greater role than natural ecosystems. Disappearance of sensitive organisms is due to direct changes in biocenoses structure, and indirect impact of humans on organisms through affecting of soil conditions and the quality of water and air. Antropopresive and biodiversity effects, thereby biodiversity reducing, it among other things, the successive: every year decrease the surface occupied by natural ecosystems and agroecosystems (Table 1) as a result of the impact of industry urbanization, expansion of communication networks, etc.

Table 1

Surface structure of soil utilization in Poland [%] [6, 7]

Specification	Years		
	1998	2008	2020
Arable land	59.4	60.9	51.5
Forests	29.0	30.3	33.4
Sweet water	2.7	2.0	2.8
Buldings	3.3	4.8	4.4
Others	5.6	2.0	7.9
Total	100.0	100.0	100.0

Maintaining the proper character of meadow communities, and therefore the maintenance of meadow biodiversity of flora and fauna requires an adequate pratotechnics (care treatments, mowing, grazing, etc.). The research was carried out in the meadow communities on the fen soil of polder in Cedynski Park after 5 years’ exclusion from showed that land expansion was by a few dicotyledonous species [8]. From stabilized, differentiated floristically communities has created a monoculture, such as tansy (*Tanacetum vulgare*).

On meadows, maintain biodiversity is very important. In other study [9] in regard to different biodiversity to be the richest community on the object cut with the height of 12 cm. on which there were 47–76 species of vascular plants (Table 2).

Table 2

The number of plants depending on the mowing height [9]

Mowing height [cm]	Number of plant species [no. · m^{-2}]	
	Rate	Mean
Initial evaluation	25–33	30 b
Without mowing	22–30	24 a
3	23–27	25 a
6	31–42	36 b
9	39–51	45 b c
12	47–76	62 c

It should be noticed that before the experiment was established the meadow species diversity had been maintained at a level between 25 to 33 species – despite the absence of any pratotechnical treatments. But, further stop-treatments (mowing), on control object, caused a reduction in the number of species to the level of 22–30 units.

In turn. the fewest species of vascular plants were by mowing at a height of 3 cm. The falling number of plants was caused by the fact that not all species tolerate such low mowing.

The research [10] shows that the number of weeds (Table 3) existing in the crop rotation (58.3 units · m^{-2}) was approximately 60 % higher than that identified in the monoculture (37 units · m^{-2}).

Table 3

Weeds number in lowland of lentis [no. · m^{-2}] [10]

Year	Rotation		Monoculture		Mean		Mean [years]
	Full cultivation	Simple cultivation	Full cultivation	Simple cultivation	Full cultivation	Simple cultivation	
1997	24.3	25.9	31.9	26.9	40.8	54.5	27.3
1998	44.0	115.5	32.4	31.5			56.0
1999	62.1	90.2	46.8	41.5			60.2
2000	54.3	49.4	30.3	54.6			47.2
Mean for years	46.3	70.3	35.3	38.7			47.7
Mean	58.3		37.0				
$LSD_{0.05}$	For cultivation – 10.9 For years – 20.5						

Number of weeds on the objects with simplified tillage (54.5 units · m^{-2}) was about 33 % higher than on the objects with a full crop (40.8 units · m^{-2}) and therefore, the crop rotation and simplified farming increased slightly floras biodiversity infestation.

Biodiversity of agrophitocenoz was also increased by intercrops which reduced the adverse effects of a uncorrect rotation of crops, particularly in the cultivation of plants in monoculture. Intercrops fill ant erosion functions and are a part of biological sorption. It was also found that the plants positively affected the quantity, biodiversity and activity of soil microorganisms [11].

The antropopresive results in environmental agriculture are so strong that, in modern strategies for sustainable development of agriculture is necessary to occurrence in the agricultural landscape of enclaves with natural community, what is realized by actions of agroecosystems biodiversity promotion. Biodiversity of agrophitocenozes depends on a large scale of agriculture system. Ecological and sustainable agriculture aspire to maintain and even increase the potential production of habitats. It is possible while is maintaining a diversified agricultural landscape and maintain heterogeneous agrocenozes. Therefore the spatial and temporal diversity of crops plays significant role. The soil in these systems of management has greater microbial biomass and greater biological activity. Interspecies mixtures as well as intergenus and intervarieties ones are important for increasing biodiversity of crop lowland. In numerous studies [12–14] the appropriate selection of species and varieties of plants for such mixtures positively affect of the quantity and quality of yield.

In addition in agroecosystems apart from crops there are weeds and saprophytic organisms, pathogens, pests and others that affect their biocenosis shape. Weeds enrich biodiversity of the field and their unfavorable effects depend on the species composition and abundance, as well as habitat conditions. If the abundance of weeds is below the threshold of harmfulness and does not increase the supply of diasporas in the soil then they are a positive element of agroecosystems.

The agrochemical treatments performed influenced the number of occurring weeds. including the application of herbicides. Many studies [15] have shown that the use of increasing doses of Chwastox extra in the cultivation of spring barley (Table 4) resulted in a systematic decrease in the number of weeds, both from the group of monocotyledons and dicotyledons.

Table 4

Structure of spring barley infestation [no · m^{-2}] after herbicide application [15]

Weeds	Mechanical cultivation	Chwastox extra 300 l SL	Chwastox extra 300 l SL	Chwastox extra 300l SL
		2 l/ha	3.5 l/ha	3 × 3.5 l/ha
Monoacyledones	31.0	24.0	19.5	10.0
Dicotyledones	13.5	2.5	1.5	1.0
Other	1.0	2.0	0.0	0.5
Total	45.5	28.5	21.0	11.5

In compare to the mechanical control, the application of the herbicide greatly reduced the dicotyledonous weeds (from 13.5 to 1.0 no. · m^{-2}) the monocotyledonous ones (from 31.0 to 10.0 no. · m^{-2}). Similar dependencies were obtained in the other experiment [13] on weed control in potato (Table 5), with increasing doses of Sencor 70WG herbicide. The number of the monocotyledons decreased from 52.0 to 21.5 no. · m^{-2} and among the dicotyledonous weeds from 5.5 to 0.5 n.o · m^{-2}.

Table 5

Structure of spring potato infestation [no. · m^{-2}] after herbicide application [15]

Weeds	Mechanical cultivation	Sencor 70WG	Sencor 70WG	Sencor 70WG
		0.5 kg/ha	1.0 kg/ha	1.5 kg/ha
Monoacyledones	52.0	24.5	17.5	21.5
Dicotyledones	5.5	3.03	1.81	0.5
Other	3.0	0.50	1.0	1.5
Total	60.5	28.03	20.31	23.5

Active substances of applied herbicides: Chwastox exstra 300 SL – MCPA; Sencor 70 WG – metrybuzyne.

The research carried out on the permanent meadow and connected with common dandelion control [16] showed that the number of dandelion per 1 m^{-2} of meadow in regrowth was from 132 to 207 plants. However, after various treatments of the dandelion control showed significant reduction of this species up to 57 no. · m^{-2}. Dandelion was eliminated from the sward after the use of herbicides, and it's number reached about 60 %. But, the mechanical methods eliminated the plant species in the share 34–36 %. Therefore, in order to maintain the common dandelion in meadow sward with a partial reduction of occurrence primarily mechanical methods should be used, because the chemical methods can eliminate this species from the sward in a very short time.

Table 6

The degree of elimination of the common dandelion from meadow sward as a result of different methods application in weed control [16]

Method of control	Number of plants per 1 m^2 I regrowth	Number of plants per 1 m^2 II regrowth	Efficiencies of control [%]
Starane – herbicide	207	82	60.3
Bofix – herbicide	204	83	60.0
Mniszek – herbicide	145	57	60.4
Ranczo – herbicide	185	78	58.1
Method by cuutting	161	103	36.0
Method by drawing	132	87	34.0

In numerous studies [17–19] it was presented that weeds protect the soil against wind and water erosion and losses of nutrients not used by plants, and their biomass increases the amount of organic matter in soil.

For the protection of biological diversity a priority task is to prevent the species existing in the wild state from existing. Over the past hundred years many wild species of plants have disappeared as well as their unique genotypes. Most of the genous stores of plants is within the populations of crop species assessed in terms of genetic diversity on the basis of the number of registered varieties. For example the register of varieties of agricultural crops from the year 2008 shows more than 1100 varieties of plant crops, large part of which come from outside of our country [1]. In addition, the fragmented and extensive agricultural economy has survived to this day, many local, old varieties of cereals, vegetables, fodder plants and fruit trees. among which there are also varieties with relict character (false flax, oily variety of common redish, true millet.

Conclusion

Disappearance of sensitive organisms is due to direct changes in biocenoses structure, and indirect impact of humans on organisms by affecting soil conditions and the quality of water and air.

On the number of occurring weeds influenced the agrochemical treatments performed, which include the application of herbicides. In compare to the mechanical control, the application of the herbicide reduced greater the dicotyledonous weeds than monocotyledonous.

In order to maintain the common dandelion in meadow sward with a partial reduction of the occurrence should be used primarily mechanical methods, because the chemical methods in a very short time can eliminate this species from the sward.

The fragmented and extensive agricultural economy has survived to this day, many local, old varieties of cereals, vegetables, fodder plants and fruit trees, among which are also a variety with relict character.

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ODDZIAŁYWANIE SYSTEMÓW ROLNICZYCH NA BIORÓZNORODNOŚĆ

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Abstrakt: Jeżeli różnorodność biologiczną mierzyć stopniem zachowania pierwotnie występujących na danym terenie gatunków oraz zbiorowisk a także form roślin i ras zwierząt użytkowych, nasz kraj można uznać za obszar o relatywnie wysokiej bioróżnorodności. Gatunki silnie zagrożone w innych krajach, zwłaszcza Europy Zachodniej występują u nas dość licznie. Wiele gatunków roślin i zwierząt osiąga na obszarze Polski granicę zasięgu występowania. To właśnie na skutek rozdrobnienia gospodarki rolnej zachowało się w Polsce jeszcze sporo lokalnych odmian roślin oraz ras zwierząt gospodarskich. Mimo to, znaczna część naszej flory jest zagrożona wyginięciem, a czerwone listy gatunków wydłużają się niemal z roku na rok.

Zdaniem wielu autorów bioróżnorodność krajobrazu rolniczego, jak i agroekosystemów, jest mniejsza niż ekosystemów naturalnych. Ustępowanie organizmów wrażliwych na antropopresję wynika z bezpośrednich zmian struktury biocenozy, jak również pośredniego oddziaływania człowieka na organizmy poprzez kształtowanie warunków glebowych oraz wpływ na jakość wody i powietrza.

Na liczbę występujących chwastów duży wpływ mają wykonywane zabiegi agrochemiczne, do których należy stosowanie herbicydów. Stosowanie wzrastających dawek Chwastoxu exstra w uprawie jęczmienia jarego powodowało systematyczny spadek liczby chwastów zarówno z grupy jednoliściennych, jak i dwuliściennych. Z kolei celu zachowania mniszka pospolitego w runi przy częściowym ograniczaniu jego występowania należy stosować przede wszystkim metody mechaniczne, gdyż metody chemiczne w bardzo krótkim czasie mogą wyeliminować ten gatunek z runi.

Słowa kluczowe: bioróżnorodność, chwasty, użytki zielone

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COMPARISON OF MERCURY CONTAMINATION IN BRED AND WILD CARPS (*Cyprinus carpio* Linnaeus 1758) CAUGHT IN AN OXBOW LAKE OF THE VISTULA RIVER

PORÓWNANIE SKAŻENIA RTĘCIĄ KARPI (*Cyprinus carpio* Linnaeus 1758) HODOWLANYCH I DZIKICH POCHODZĄCYCH ZE STARORZECZA WISŁY

Abstract: Presence in meat of the fish of the toxic substances motivates to the undertaking of investigations can the scale of the wholesome threat for the man (angler), which he stood from the right of hunting of the fish oneself the final link in the chain trophic of water ecosystem in this also in the process of the accumulation of heavy metals. The comparison of the degree of the contamination was the generally basic aim of investigations carps mercury and the settlement, what influence on her postponing, and every he goes for this, what there is the threat toxicological for angler fishing the fish of the same species in natural reservoir or animal pond. They made up the material to investigations carps gain over from two various water environments after 10 of every one the clatter in seasons 2004–2006 years. The content of mercury in taken tests was studied use the automatic analyzer of the traces of the mercury of AMA 254 in support about the method of the *absorption of atomic spectrometry* (AAS). The degree of the mercury contamination studied ponds carps was low and many the times lower than admissible norms of hygienic. Carps coming from the old flood water of the Vistula river contain in their tissues and organs the larger quantities of mercury, what to result from the larger dirt of waters of the Vistula in this heavy metal. The average concentration the mercury in the carps studied group wild it was twice lower than admissible hygienic norms.

Keywords: breeding carps, wilds carps, contamination, mercury

The element mercury (Hg) and its compounds have no known normal metabolic function. Their presence in the cells of living organisms represents contamination from natural and anthropogenic sources; all such contamination must be regarded as undesirable and potentially hazardous.

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Mercury is a naturally occurring metal, a useful chemical in some products, and a potential health risk. Mercury exists in several forms – the types people are usually exposed to are methylmercury and elemental mercury. Elemental mercury at room temperature is a shiny, silver-white liquid, which can produce a harmful odorless vapor. Methylmercury, an organic compound, can build up in the bodies of long-living, predatory fish. To keep mercury out of the fish we eat, it's important to take mercury-containing product to a hazardous waste facility for disposal [1].

Inorganic mercury washed into water bodies is converted to an organic form, methylmercury, by the action of microbes. Mercury contaminated plankton is eaten by small fish and increasingly large fish feed on them. Higher rates of methylation are found in acidified waterbodies (low pH), and sulfates from acid rain may also accelerate methylation. There is some indication that smaller, warmer, more eutrophic bodies have higher rates of methylation. Methylmercury is the element's most toxic form; it not only accumulates in the aquatic food chain but tends to concentrate strongly as it is passed upward in the food chain. Thus methylmercury concentrations in predator fish can be a million times higher than those of the surrounding water. Mercury binds strongly with sulfhydryl groups. The sulfhydryl groups within cysteine function to form "cross-links" or disulfide bridges between two cysteines. These cross-links are what give proteins three-dimensional structure. When mercury binds to the sulfhydryl groups, the disulfide bonds are broken and the protein loses its structure and is rendered non-functional.. It has many potential target sites during embryogenesis; phenylmercury and methylmercury compounds are among the strongest known inhibitors of cell division. Organomercury compounds, especially methylmercury, cross placental barriers and can enter mammals by way of the respiratory tract, gastrointestinal tract, skin, or mucous membranes. When compared with inorganic mercury compounds, organomercurials are more completely absorbed, are more soluble in organic solvents and lipids, pass more readily through biological membranes, and are slower to be excreted [1, 2].

A wide range of adverse health effects have been observed in humans following methylmercury exposure, the severity largely depending on the magnitude of the dose and the duration of exposure. The predominant health affects in humans are associated with the impaired functions of the central and peripheral nervous systems. For example, elevated methylmercury exposure in a fetus or young child can cause a decrease in I.Q., delays in walking and talking, lack of coordination, blindness, and seizures. In adults, excessive methylmercury exposure can lead to personality changes, tremors, changes in vision, deafness, loss of muscle coordination and sensation, memory loss, intellectual impairment, and, in very extreme cases, even death [1–4].

Mercury is present in surface waters in both inorganic and organic forms; the latter mainly as methylmercury. This compound easily enters the aquatic food chains. Predatory fish as the last link in this chain may concentrate in their tissues 1–10 million times more mercury than that present in water [1–3]. It is assumed that 90–100 % of mercury in adult fish is bound with methyl group. Combined with sulfhydryl (-SH) groups in proteins mercury occurs mainly in fish muscles. It enters fish organism in three ways: through gills, skin and alimentary tract [1, 3, 5].

Boiling, frying or any other way of thermal processing does not decrease mercury content in fish. On the contrary, its concentration increases proportionally to the loss of water during preparation. Mercury from protein structures is not removable during these processes.

From among all types of food in human diet most contaminated with mercury are fish, crustaceans and other *frutti di mare* in which mercury concentration may be 10^3–10^4 times higher than in vegetables, fruits, meat, eggs or milk [1, 2].

Mercury poisoning has usually been associated with large ocean fish, such as shark, swordfish, king mackerel, tilefish or tuna. But the freshwater fish most likely to contain harmful amounts of mercury include smallmouth bass, walleye, largemouth bass, lake trout and pike. Freshwater fish are more likely to be contaminated than ocean fish. A report from the *Environmental Protection Agency* (EPA), showed that virtually every freshwater fish sample tested from lakes across the United States was contaminated with mercury. About 55 % samples of freshwater fish contained mercury levels that exceeded EPA's "safe" limit for women who eat fish twice a week, particularly those in their child-bearing years and 76 % of the fish sampled contained mercury levels that exceeded the EPA's safe limit for children under age three who eat fish twice a week. [2, 3].

Studies on mercury content in the tissues of fish from the middle course of the Vistula River carried out since the beginning of the 1990's indicate systematic decrease of mercury concentration [6]. This is true for all heavy metals delivered to the Baltic Sea with river waters in the years 1995–2007. For example, the annual load of chromium decreased from 48.7 to 15.6 Mg, that of lead – from 124.7 to 68.9 Mg [7]. The load of mercury varied, however, from 9 $\mathrm{Mg \cdot yr^{-1}}$ in 1995 to 0.6 $\mathrm{Mg \cdot yr^{-1}}$ in 2004 to increase again in 2007 to 17.8 $\mathrm{Mg \cdot yr^{-1}}$ [7]. The total lack of the measurements of the rigors of heavy metals in the measuring point in Kiezmark on Vistula River, and also in some rivers of near Baltic Sea makes impossible the realization of the comparative analysis in the relation till next years after 2007 [7, 8].

At present, there are nearly 1.5 million active anglers in Poland including 600 thousand members of the Polish Angling Association and their families. Specialists estimate that anglers catch annually 40–50 thousand Mg of fish which makes c. 35–80 kg of fish per person. Angling means not only fish catching but also nature protection and tourist development of the region. And finally, health aspect should also be mentioned since economic and technological development may be detrimental to human health. The presence of contaminants in fish justifies the studies undertaken to estimate the degree of health risk for angler who, by catching fish, becomes top predator in the food chain of aquatic ecosystem and thus participates in the process of heavy metal accumulation. The aim of this study was to compare fish contamination by mercury and toxicological risk posed to an angler catching fish of the same species in the natural water body and in fish pond.

Material and methods

Carps (*Cyprinus carpio* Linnaeus 1758) for this study were obtained from two aquatic habitats (10 individuals from each) in the years 2004–2006. Fish were caught in an oxbow lake near Czerwinsk on Vistula (most common in Europe full scaled carps) and in ponds of the Fishery Station SGGW in Jaktorow (mirror carp). Before sampling tissues and organs of these fishes were weighed and measured. Caught fish had a mass between 500 and 1430 g and length between 27 and 39 cm. Samples of upper muscles, gills, hepato-pancreas, middle intestine, kidneys, gonads and scales were taken from each fish and kept deep frozen until analyses.

The content of mercury was determined using atomic absorption spectrophotometry with the computer controlled automatic mercury analyzer AMA 254 made by Altec (CR). The method consists in the measurement of absorption spectrum of a lamp with cathode made of mercury. Sensitivity is 0.01 ngHg $\cdot$ kg^{-1} and measurement range 0.05–600 ng. Maximum mass of the sample should not exceed 300 mg. The entire analytical procedure was validated by analyzing reference material No. 422 Cod Muscle (lyophilised) samples at the beginning and end of each set of tissue samples.

Concentration of mercury is given in mg $\cdot$ kg^{-1} of the tissue mass. Each measurement was triplicated and results are given as means. The apparatus was calibrated with the solution of polarographically pure mercury in 2 % HNO_3. Arithmetic mean, standard deviation, minimum and maximum values were calculated and results were statistically processed using the computer program Statgraphic 4 .

Results and discussion

The highest concentrations of mercury (mean 0.2548 mg $\cdot$ kg^{-1}) were found in muscles of wild full scaled carps. The concentration in muscles of bred mirror carps was nearly three times lower (0.0775 mg $\cdot$ kg^{-1}). However, maximum concentration of 0.5247 mg $\cdot$ kg^{-1} found in the largest wild carp exceeded the maximum tolerable limit of mercury established at 0.5 mg $\cdot$ kg^{-1} for bottom feeding fish [9]. It is particularly alarming since the biomass of wild carps was twice lower than the biomass of bred carps. Having in mind that the growth rate of wild carp is nearly two times slower one may assume that analyzed fishes could be of the same age. Higher concentrations of mercury were also noted in other tissues and organs of wild carp as compared with bred carp (Tables 1 and 2).

Table 1

Concentration of mercury in tissues and organs of wild carp (*C. carpio*) from the Vistula River oxbow lake [mg $\cdot$ kg^{-1}]

Parameter	Mass [g]	Length [cm]	Scales	Gills	Hepato-pancreas	Kidney	Gonads	Muscles
Mean	670	29.6	0.0084	0.0185	0.0536	0.0762	0.0217	0.2548
Standard deviation	190.8	2.72	0.0039	0.0095	0.0418	0.0317	0.0127	0.1810
Minimum	500	25	0.0038	0.0019	0.0122	0.0351	0.0187	0.1472
Maximum	980	35	0.0152	0.0394	0.1162	0.1126	0.0217	0.6247

Table 2

Concentration of mercury in tissues and organs of bred carp (*C. carpio*) from ponds in the Fishery Station SGGW in Jaktorow [mg · kg^{-1}]

Parameter	Mass [g]	Length [cm]	Scales	Gills	Hepato-pancreas	Kidney	Gonads	Muscles
Mean	1268	36.4	0.0122	0.0098*	0.0197**	0.0294*	0.0088*	0.0775**
Standard deviation	131.3	2.02	0.0039	0.0019	0.0044	0.0138	0.0026	0.0121
Minimum	1080	34	0.0068	0.0078	0.0134	0.0198	0.0060	0.0593
Maximum	1430	39	0.0191	0.0156	0.0230	0.2334	0.0157	0.1019

Explanations: differences in the concentration of mercury between two groups of carps significant at * $p < 0.05$, ** $p < 0.01$.

The lowest mercury concentrations were found in gonads of fish from both races. This regularity was also noted in breams from the Vistula River and was explained by the protection of reproductive organs from genotoxic and teratogenic effect of mercury [6].

Carps caught in the oxbow lake of the Vistula River basin and analyzed within this study were relatively small as compared with the size carp may achieve in the wild. Since contamination with mercury increases linearly with fish weight and age, one may expect that larger individuals contain more mercury which eventually would exceed the tolerable threshold concentration.

This does not concern fish from fish farms which allow anglers to use their ponds for that form of recreation. To intensify carp production in cultures fish are given concentrated food composed of seeds of legume and cereal plants and granulated proteins. Moreover, ponds are usually filled with water of controlled quality. Taking all this into account, and relatively short (2–3 years) productive cycle in bred carps, significant contamination by mercury is less probable in this case.

The literature suggests that in our study, mean Hg concentration are lower than those reported for carp (0.70 mg · kg^{-1}) in the Nitra River in Slovakia [10]. In contrast, mean Hg levels in carp muscles in the present study are higher than those described for Ya-Er Lake in China (0.08 mg · kg^{-1}) [11].

Fish is an important part of healthy diet. It is a good protein source that is low in saturated fats and high in beneficial omega-3 fatty acid and other nutrients. Fish consumption decreased the risk of cardiovascular disease. Other reported benefits of fish consumption include a decrease in some cancers and protection against declines of brain function [1, 3, 4] Our results of the fish tissue analysis indicate that bred carp and carp from the oxbow lake in the Vistula are generally low in mercury concentration and do not require meal limit advice.

Conclusions

1. The degree of contamination by mercury in bred carp is many times lower than the acceptable hygienic standard.

2. Carps from the oxbow lake in the Vistula valley contain more mercury in their tissues and organs, probably because of higher concentration of this metal in river waters.

3. Mean concentration of mercury in the group of wild carps was two times lower than the acceptable hygienic standard.

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PORÓWNANIE SKAŻENIA RTĘCIĄ KARPI (*Cyprinus carpio* Linnaeus 1758) HODOWLANYCH I DZIKICH POCHODZĄCYCH ZE STARORZECZA WISŁY

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Abstrakt: Obecność w mięsie ryb substancji skażeniowych uzasadnia podjęcie badań mogących ustalić skalę zagrożenia zdrowotnego dla człowieka (wędkarza), który z racji łowienia ryb stał się końcowym ogniwem w łańcuchu troficznym ekosystemu wodnego w tym również w procesie kumulacji metali ciężkich. Generalnie podstawowym celem badań było porównanie stopnia skażenia rtęcią karpi i ustalenie, jaki wpływ na jej odkładanie, a co za tym idzie, jakie jest zagrożenie toksykologiczne dla wędkarza łowiącego ryby tego samego gatunku w akwenie naturalnym lub stawie hodowlanym. Materiał do badań stanowiły karpie pozyskane z dwóch różnych środowisk wodnych po 10 stuk z każdego w sezonach 2004–2006 Zawartość rtęci w pobranych próbkach badano przy użyciu automatycznego analizatora śladów rtęci AMA 254, wykorzystując metodę spektrometrii absorpcji atomowej (AAS) Stopień skażenia rtęcią badanych karpi hodowlanych był niski i wielokrotnie niższy od dopuszczalnych norm higienicznych. Karpie pochodzące ze starorzecza Wisły zawierają w swych tkankach i narządach większe ilości rtęci, co może wynikać z większego zanieczyszczenia wód wiślanych tym metalem ciężkim. Średnie stężenie rtęci w badanej grupie karpi dzikich było dwukrotnie niższe od dopuszczalnych norm higienicznych.

Słowa kluczowe: karpie hodowlane, karpie dzikie, skażenie, rtęć

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EFFECT OF FOLIAR SULPHUR FERTILIZATION ON THE PRODUCTIVITY OF THE PERMANENT AND ALTERNATE MEADOW
PART II. THE CONTENT OF MICROELEMENTS

WPŁYW DOLISTNEJ APLIKACJI SIARKI NA PRODUKCYJNOŚĆ ŁĄKI TRWAŁEJ I PRZEMIENNEJ
CZ. II. ZAWARTOŚĆ MIKROELEMENTÓW*

Abstract: The experiment was established by means of random block sampling in four replicants on the brown acid soil of V quality class. The study was conducted in the years 2006–2008 on an individual farm in Pilica administrative district, in Zawiercie county, in the region of Krakow–Czestochowa Jura, at the altitude of above 320 m.

Foliar sulphur fertilization of the sward of the permanent and alternate meadows was the determination factor. After the mineralization the hay samples were subjected to the analysis of Zn, Cu, Fe and Mn by ICP-AES method. The effect of sulphur fertilization on the level of selected elements in the plant samples collected from the permanent and alternate meadow was estimated.

The weighted mean content of elements in plants derived from both meadows fluctuated in the range of: 22.81–224.86 mg Zn; 3.82–16.67 mg Cu; 60.90–190.35 mg Fe; 19.58–151.37 mg Mn $\cdot$ kg^{-1} d.m.

It was stated that applied fertilization had the most spectacular effect on the zinc content in both meadow types and on the iron content in the case of permanent meadow. In our investigations we observed that the herbs were the richest in microelements. The grasses were characterized with the lowest content of these elements with the exception of the manganese level higher in grasses from the fields non-fertilized with sulphur than in leguminous plants.

Keywords: meadow sward, sulphur fertilization, content, microelements

Sulphur is a very important nutrient and its proper supply affects the proper growth and development of plants [1–3]. As sulphur is a component of essential amino acids like: cysteine, cystine and methionine, its deficiency can lead to the decrease of protein synthesis. Moreover, this element can be found in many enzymes responsible for the

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proper proceeding of metabolic pathways. It also takes part in the process of the nitrate reduction, atmospheric oxygen binding as well as regulation of chlorophyll synthesis in chloroplasts. Critical sulphur content, below which the inhibition of grass development may occur is equal to 1.0 g and the respective value for clover amounts to 2.5 g $S \cdot kg^{-1}$ d.m. The total sulphur content in the forage destined for ruminants should fluctuate in the range of 1.8 to 3.0 $g \cdot kg^{-1}$ d.m. [4].

The adjustment to the requirements of environmental protection led in recent years to the significant reduction of SO_2 release into the atmosphere, which resulted in lower sulphur concentration in soil. Therefore, the application of sulphur fertilizers is needed because sulphur which is the accidental component of mineral fertilizers cannot cover the plant demand for this element [5]. Moreover, deficiency of sulphur in the soil affects lower level of nitrogen assimilation from the applied fertilizers, which can be dangerous for natural environment [6]. On the basis of the investigations, it was stated that the 3:1 P_2O_5:S as well as 5:1 N:S weight proportions are beneficial for achieving the most effective phosphorus and nitrogen (respectively) action [7].

The beneficial effect of sulphur on the plant condition has been confirmed by the results of many studies [8–10], but to ensure the efficiency of fertilization during the whole vegetation period, the form and amount of the element applied is very important.

The aim of the present study was an estimation of the effect of sulphur foliar application on the content of microelements in permanent and alternate meadow flora.

Materials and methods

The investigations were conducted in the years 2006–2008, in the individual farm located in Pilica administrative district, in Zawiercie county, in the Silesia province, at the altitude of 320 m. The study was established by means of random block sampling in four replicants, on the brown, acid soil (pH_{KCl} = 5.2) of the V quality class. The investigated objects were located on the permanent and newly-established alternate meadow during the second year of the full utilization. The soil contained medium levels of assimilable potassium, manganese and zinc and low levels of phosphorus and copper. During the vegetation period (IV–IX) total rainfall and average air temperatures for each year of the study were as follows: 2006 – 338 mm and 15.2 °C; 2007 – 375 mm and 14.3 °C; 2008 – 320 mm and 14.9 °C.

Foliar fertilization with sulphur constituted the determining factor in the study. Foliar fertilizer in the form of Super S-450 suspension in a dose of 2 $dm^3 \cdot ha^{-1}$ (equal to 900 $g\ S \cdot ha^{-1}$) was applied under each regrowth.

In each year of the experiment the following mineral fertilization was used for both meadow types: under the first regrowth – 80 $kg\ N \cdot ha^{-1}$, under the second and third regrowths – 60 $kg\ N \cdot ha^{-1}$ (for each regrowth) in the form of ammonium saltpetre, phosphorus – once in the spring, in the amount of 120 $kg\ P_2O_5 \cdot ha^{-1}$ in the form of triple superphosphate and potassium – under the first and third regrowths – 60 $kg\ K_2O \cdot ha^{-1}$ (for each regrowth) in the form of 57 % potassium salt. The experimental fields were characterized with the area of 10 m^2. Collected plant samples were subjected to the analysis of the forage chemical composition. Dry matter content was determined by the drying method at 105 °C. The plant trials were mineralized using the dry process in the muffle oven at 450 °C [11]. The content of Zn, Cu, Ni, Fe and Mn was determined by ICP-AES (*inductively coupled plasma-atomic emission spectrometry*) method.

The obtained results were subjected to the statistical analysis of variance. Mean values were compared on the basis of the results of the Duncan test at the significance level of 0.05.

Results and discussion

Our investigations revealed that the permanent and alternate meadow fertilization with sulphur significantly affected the chemical composition of the meadow flora. Foliar application of the sulphur fertilizer had the most spectacular effect on the zinc content in the meadow plants (Table 1).

Table 1

Weighted mean content of microelements [mg · kg^{-1} d.m.] in examined plant groups as affected by the sulphur fertilization (means of three years)

Species	Permanent meadow				Alternate meadow			
	Zn	Cu	Mn	Fe	Zn	Cu	Mn	Fe
Series without sulphur (–S)								
Grasses	22.81a*	3.82a	25.36b	60.90a	24.68a	4.67a	45.86b	72.90a
Legumes	26.56ab	7.82c	19.58a	83.90b	38.84ab	8.87bc	26.97a	90.05b
Herbs and weeds	33.98b	12.44cd	27.45b	151.48cd	46.42b	13.81c	75.70c	136.41c
Meadow sward	26.47a	5.43b	26.37b	98.70b	44.10b	4.42a	62.50bc	103.20bc
Series with sulphur (+S)								
Grasses	32.87b	5.35b	38.33bc	94.90b	47.54b	5.26a	71.88c	101.00bc
Legumes	116.54c	8.33c	75.78cd	98.40b	199.07cd	11.08bc	73.75c	117.80bc
Herbs and weeds	136.48d	14.62d	85.74d	183.23d	224.86d	16.67cd	151.37d	190.35d
Meadow sward	30.93b	7.35c	29.05b	154.90cd	65.93bc	6.90b	71.80c	105.60bc

* Means marked with the same letter are not statistically different following verification with Duncan test (P = 0.05).

The highest zinc level was stated for the plants collected from the object treated with sulphur fertilizer. In this case the plants from the permanent meadow were characterized with 65 % higher zinc content than plants collected from the non-fertilized object. The respective increase of the zinc level in the plants from the alternate meadow amounted to 71 %. As the result of sulphur foliar application significant increment of the average magnesium content was stated when compared with the control object. The difference amounted to 57 and 43 % respectively for the permanent and alternate meadow. A similar effect of this treatment was observed in the case of average copper content. The level of this element was respectively 17 and 20 % higher for the permanent and alternate meadow fertilized with sulphur. Also the iron content was positively affected by the sulphur fertilization of the meadow sward, which contained 26 (for permanent meadow) and 22 % (alternate meadow) higher concentration of this element. The obtained results are in some part consistent with the results reported by Kulczycki [12], Kaczor et al [13], Brodowska [14], who stated that sulphur plays an important role in plant metabolism, influencing their chemical composition, what in turn directly affects the quality of crops.

According to established requirements, the amounts of microelements in forage that cover the animals feeding demand are as follows: Zn – 50 mg; Cu – 10 mg; Fe – 50 mg and Mn – 60 mg $\cdot$ kg^{-1} d.m. [15, 16]. In that light, it can be found from present study that foliar application of sulphur had a beneficial effect on the content of microelements (an increased level when compared with plants from the control object) in all examined plant groups. Higher concentrations of nutrients as a result of sulphur fertilization are also reported by other authors [9, 16].

Our investigations revealed that among all examined species herbs were the richest in microelements. On the contrary, grasses contained the lowest level of these components with exception of manganese content higher than its level in leguminous plants.

Conclusions

1. Application of sulphur fertilization had the most visible effect on the zinc and manganese content. Foliar fertilization with sulphur caused significant growth of mean zinc content on the permanent and alternate meadow by 65 and 71 %, respectively. The respective increase of manganese content amounted to 57 and 43 %.
2. Sulphur fertilization led to a 17 and 20 % (respectively) higher copper level on the permanent and alternate meadow.
3. Application of the sulphur fertilizer resulted in respectively 26 and 22 % higher iron content in the samples derived from the permanent and alternate meadow.
4. Our investigations revealed that among all examined species herbs were the richest in microelements, whereas grasses contained the lowest level of these components.

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WPŁYW DOLISTNEJ APLIKACJI SIARKI NA PRODUKCYJNOŚĆ ŁĄKI TRWAŁEJ I PRZEMIENNEJ

CZ. II. ZAWARTOŚĆ MIKROELEMENTÓW

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Abstrakt: Doświadczenie polowe założono metodą losowanych bloków w czterech powtórzeniach na glebie brunatnej kwaśnej, zaliczonej pod względem bonitacyjnym do klasy V. Doświadczenie prowadzono w latach 2006–2008, w indywidualnym gospodarstwie rolnym położonym w gminie Pilica, powiat zawierciański na Jurze Krakowsko-Częstochowskiej, na wysokości powyżej 320 m n.p.m.

Czynnikiem doświadczenia było dolistne nawożenie siarką runi łąki trwałej i przemiennej. Po mineralizacji próbek siana oznaczono zawartość Zn, Cu, Fe i Mn metodą ICP-AES. Oceniano wpływ nawożenia siarką na zawartość wybranych pierwiastków w roślinność łąki trwałej i przemiennej.

Średnia ważona zawartości wybranych pierwiastków w roślinności obu łąk wahała się w zakresie: 22,81–224,86 mg Zn; 3,82–16,67 mg Cu; 60,90–190,35 mg Fe; 19,58–151,37 mg Mn $\cdot$ kg^{-1} s.m.

Wykazano, że zastosowane nawożenie największy wpływ wywarło na zawartość cynku na obu typach łąki oraz żelaza na łące trwałej. W badaniach własnych stwierdzono, że największą zasobnością w mikroelementy cechowały się zioła. Trawy zawierały najmniej badanych mikroelementów, jedynie manganu miały więcej niż rośliny motylkowate, ale tylko na obiektach nienawożonych siarką.

Słowa kluczowe: ruń łąkowa, nawożenie siarką, zawartość, mikroelementy

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DETERMINATION OF BARIUM IN DIFFERENT SOIL MATRICES

OZNACZANIE BARU W RÓŻNYCH MATRYCACH GLEBOWYCH

Abstract: Barium mobility and toxicity depend on the speciation forms in which barium occurs in a given environment. The dominant form is the carbonate – barite one. There are also other significant forms in this element's cycle – the organic one, so-called reduced or lithogenic. The speciation forms of occurrence and their amount in soils and solid waste may be assessed using sequence extraction. The subject of the paper was to carry out research on the determination of so-called barium fractions in various soil matrices: agriculturally utilized or used for recreation, polluted with motor vehicles and soil-waste contaminants (from brown coal and bituminous shales recovery). On the basis of the present research, the individual barium loads existing in various fractions – exchangeable, carbonate, reduced, organic and residual – were determined. In research procedures, Tessier's methodology was used for sequence extraction.

Keywords: barium, barium speciation forms in soils and waste, sequence extraction

Barium is an element which occurs in the barite form ($BaSO_4$) and the witherite one ($BaCO_3$) [1–4]. The range of its content, *eg* in magmatic rocks ranges from 0.5–1200 mg/dm^3 and is higher than in acidic rocks while in sedimentary rocks it is dispersed in the range 50–800 mg/dm^3, indicating the tendency to concentrate in the mudstone [1]. In soils, this element migrates together with circulating waters and is leached inside the soil profile (mainly in the form of aqua complexes $[Ba(aq)_n]^{2+}$ and ion pairs $Ba^{2+} \cdot SO_4^{2-}$ and $Ba^{2+} \cdot CO_3^{2-}$) or is subject to concentration in the thin surface layer [2, 3], binding ionically and coordinating together with the contained humus substance [3]. The barium content in soils most frequently ranges from 20–1000 mg/dm^3 [1] and 1350 mg/kg in the industrial development areas [5]. The interesting problem is the analytical determination of this element's concentrations in various environmental matrices and waste substances and its speciation forms [6, 7]. It is the issue which is relatively little known, especially as far as the occurrence of functional dependencies between speciation forms and specific properties of mineral – organic matrices is concerned. From literature data we know that this issue is taken with the use of various leaching

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procedures [6, 8]. Barium speciation forms, especially the ones leached from different waste substances are the subject of interest due to the various toxicity for biocenoses [9–13].

The purpose of the work was barium fractions determination in the soils which were agriculturally utilized, used for recreation, polluted with motor vehicles and contaminated with post-mineral wastes. The obtained results were discussed and compared with literature data.

Materials and methods

Barium was determined in five extrahent solutions with the use of *flame atomic absorption spectrometry* (FAAS); the wavelength of 553.6 nm. This element's content was analyzed in soil samples (collected from sub-surface soil layer) from the vegetable garden located on the outskirts of the city (P1 – average soil, pH 7.51), farmland located near the urbanized area (P2 – heavy, pH 9.35) and from the recreational park area located near a big city (P3 – light, pH 7.56) (Table 1). The areas of taking the soil samples loaded with waste substances were: P4 – located near excavation from brown coal recovery and P5 – from bituminous shales recovery (Table 2). The remaining two series of samples came from the crossroads of the big city (P6) and the bus depot (P7) from this city. Samples P1–P3 and P6 and P7 were taken from places located on the territory of the same district self-government, and the maximum distance between collection points did not exceed 7.0 km. Samples were taken from the area of 20.0 m^2 in each case and were subject to sequence extraction in accordance with Tessier's methodology [14–17], applying air – dried surplus (40.0 g each) which was treated with extracting solutions of the increasing strength according to procedures given below:

A) fraction I. In order to determine barium content in fraction I (so-called exchangeable barium forms), samples were treated with 20.0 cm^3 (1.0 M) of $CaCl_2$ and after intensive shaking (at pH 7.0), shaken out for 1 hour at room temperature. After separating the solid components in the filtration process, the filtrate was subject to the analysis of this element's content. The residued solid soil samples were washed with distilled water and dried.

B) fraction II. Dried soil samples, which remained after running the procedure in accordance with point A, were subject to extraction (so-called barium forms bonded with carbonates – fraction II) adding 40.0 cm^3 (1.0 M) CH_3COONH_4 and acidating it with 80 % of CH_3COOH to pH 7.0.

After mixing, it was shaken for 5.0 hours at room temperature. During this operation the reaction was controlled: when $pH > 7.0$ – it was acidified. The filtrate was subject to analysis, and the washed and dried samples of the solid phase were used for the 3rd stage of extraction (to determine the so-called barium forms connected with aqueous ferric and manganese oxides).

C) fraction III. At this stage (determination of fraction bounded with Fe/Mn oxides) to the dried sample of the solid phase, residual was added and mixed after taking the procedure in accordance with point B, 40.0 cm^3 (0.04 M) solution of $NH_2OH \cdot HCl$ in

25 % CH_3COOH. Samples (pH 2.0) were shaken for 5.0 hours at the temperature of 96 ± 3 ^oC. The filtrate was subject to analysis, and the washed and dried solid material was directed to the 4th stage of extraction (so-called barium bounded with organic matter – fraction IV) to constant residues.

D) fraction IV. 10.0 cm^3 (0.02 M) HNO_3 and 10.0 cm^3 30 % aqueous solution of H_2O_2, were added to the material sample from the stage given in point C. They were mixed (pH 2.0) and shaken for 135.0 minutes at the temperature of 85 ± 2 ^oC. Next, 10.0 cm^3 30 % H_2O_2 was added and shaken for 135.0 minutes. After that time, 20.0 cm^3 (3.0 M) of CH_3COONH_4 in 20 % HNO_3 (v/v) was added and shaken for 30.0 min at the room temperature (pH 2.0). The filtrate was subject to analysis, and the residual washed and dried soil samples were subject to 5-stage of extraction (residual barium forms – fraction V).

E) fraction V. 6.0 cm^3 of HNO_3 and 4.0 cm^3 of 30 % H_2O_2, were added to the residues from the solid phase in point D, and then mixed (pH 2.0). They were shaken at the boiling point for one hour, adding HNO_3 and H_2O_2 twice until white ashes were released. Next, 20.0 cm^3 of 30 % H_2O_2 were added and shaken for 30.0 minutes at the boiling point. The results of the analyses for barium content in the individual fractions are presented in Tables 1–3.

Results and discussion

The aim was to apply Tessier's procedure to determine barium fractions occurring in the selected samples of clean soils and the soils contaminated with substances of anthropogenic origin (post-mineral wastes and motor vehicle contaminations) (Tables 2 and 3).

In soil samples taken from the same area (samples P1–P3, P6 and P7), despite the motor vehicle pollutions (samples P6 and P7), similar concentrations of the given fractions were determined (Tables 1 and 3) and no evident influence of motor vehicle traffic on the fractional content of this element was found.

Table 1

Average concentrations of barium fraction in mg/kg dry mass determined in the selected soil samples with the use of sequence extraction method*

Barium fractions	P1 samples (RSD [%])		P2 samples (RSD [%])		P3 samples (RSD [%])	
(I) exchangeable	17.76	(2.1)	42.59	(0.6)	16.18	(2.7)
(II) carbonate	31.71	(0.7)	27.21	(1.6)	29.11	(0.1)
(III) Fe/Mn oxides	10.63	(1.8)	15.64	(2.1)	8.97	(1.1)
(IV) organic	12.13	(0.9)	14.33	(1.5)	9.14	(1.9)
(V) residual	33.26	(2.0)	38.60	(3.0)	29.70	(2.5)

* P1 samples – average soil (pH 7.51), P2 samples – heavy soil (pH 9.35), P3 samples – light (pH 7.56); RSD – relative standard deviations.

Table 2

Average concentrations of barium fractions in mg/kg dry mass determined in soil samples contaminated with solid substances (mixture of post-mineral wastes and soil*) with the use of sequence extraction method

Barium fractions	P4 samples, (RSD [%])		P5 samples (RSD [%])	
(I) exchangeable	20.84	(0.8)	32.03	(0.1)
(II) carbonate	128.00	(1.2)	64.12	(0.9)
(III) Fe/Mn oxides	192.10	(1.7)	160.21	(1.3)
(IV) organic	32.13	(0.6)	31.99	(0.5)
(V) residual	284.82	(2.8)	291.22	(1.9)

* Area of taking the samples (pH 7.11) located close to post-mineral depot from brown coal recovery and clone to post-mineral depot from bituminous shales recovery (pH 6.80) (samples P7).

Table 3

Average concentrations of barium fractions in mg/kg dry mass determined in soil samples overloaded with motor vehicle pollution with the use of sequence extraction method*

Barium fractions	P6 samples (RSD [%])		P7 samples (RSD [%])	
(I) exchangeable	48.33	(1.2)	16.13	(1.2)
(II) carbonate	22.92	(2.2)	11.10	(1.8)
(III) Fe/Mn oxides	16.77	(2.4)	12.61	(2.0)
(IV) organic	14.07	(1.7)	7.93	(1.8)
(V) residual	30.59	(2.8)	20.31	(2.0)

* P6 samples – light soil (pH 6.69), P7 samples – light (pH 7.39).

Changeable fraction, which naturally occurs mainly in the form of aqua complexes $[Ba(aq)_n]^{2+}$ and ionic pairs of $Ba^{2+} \cdot SO_4^{2-}$ and $Ba^{2+} \cdot CO_3^{2-}$ were determined at the similar quantity level in soil samples of reduction pH = 7.3–7.6, mainly in light soils (samples P1, P3 and P5). In these samples, the content of the changeable fraction did not exceed 25 % of the total content of this element. The highest content of this fraction compared with the total content was determined in soil samples taken from the farmland (heavy soil) and from the crossroads; and they were respectively: 30.8 and 36.4 % at the similar, average barium content respectively: 138.37 and 132.68 mg/kg dry mass.

Assessing the barium fraction bound with Fe/Mn oxides in samples P1–P3, P6 and P7, a similar content level was found in clean samples and loaded with motor vehicle pollutions (Tables 1 and 3). Such level of the fraction compared with the iron content, particularly manganese towards oxides, for which barium shows particular preference, can be explained due to a slight distance of the sample recovery points [18–21]. However, in case of soil samples contaminated with brown coal and bituminous shale waste, high total content of this element and the specific content of the matrices (significant content of oxide iron and manganese forms) results in extremely high concentrations of this barium fraction, amounting to about 30 % of the total barium content.

The significant difference in concentrations of the given fractions for clean soils samples (Samples P1–P3) and the ones overloaded with motor vehicle pollutions (samples P4 and P5) is evident in case of organic fraction – (P4). The concentration level of this fraction for clean soils is similar, despite the different content of humus substances and at the same time 3 times lower than the one registered in case of soils polluted with waste. This phenomenon can be interpreted by the presence of high-molecular organic substances of humin type (Hum), which are present in brown coal and bituminous shales fragments contaminating the examined soil samples. The presence of these substances results in forming very constant bonds of covalent type $Ba_a(R)_b$ (where: R – organic ligand, a and b – coefficients resulting from stoichiometry rules) or to a smaller extent – the coordinating one, certainly resulting in complex structures, which can be described by a simplified formula $[Ba(Hum)_x]^{(+2-y)}$ (where: Hum – high-molecular organic ligands which are the natural humification products, x – number of coordinated ligands (Hum), y – ligand's valency) [22, 23]. From the comparison of the content level of the fraction for the given sample categories we may conclude that coordinating barium occurs under the influence of the determined class of the high-molecular organic compounds, which are many times lower than in samples P1–P3, P6 and P7 than in contaminated samples P4 and P5.

The content of the so-called residual fraction (fraction V) in the determined soil samples was different – in clean soil samples and in ones overloaded with motor vehicle pollutions it amounted to 20–30 %, and in soil samples polluted with post-mineral residues – over 40 % of the total barium content just as in drilling mud [15].

Conclusion

On the basis of the conducted research it was found that soils contaminated with post-mineral waste are characterized with a higher amount of barium determined in the fractions: bound with Fe/Mn oxides and the so-called residual one. The registered concentration of this element in organic fraction, in samples containing post-mineral residues is higher than the values registered for the rest of the soil samples. In case of soil samples overloaded with motor vehicle pollutions, no evident difference in barium fractional content was found in relation with the fractional content determined in clean soil samples.

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OZNACZANIE BARU W RÓŻNYCH MATRYCACH GLEBOWYCH

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Abstrakt: Mobilność oraz toksyczność baru zależy od form specjacyjnych, w jakich występuje w danym środowisku. Dominującą jest węglanowa – barytowa. Istnieją również inne, istotne w obiegu tego pierwiastka

– organiczna, tzw. zredukowana czy litogenna. Specjacyjne formy występowania oraz ich ilość w glebach i stałych substancjach odpadowych można oszacować, wykorzystując ekstrakcję sekwencyjną. Przedmiotem pracy były badania nad oznaczalnością tzw. frakcji baru w różnych matrycach glebowych: użytkowanych rolniczo i rekreacyjnie, obciążonych zanieczyszczeniami komunikacyjnymi oraz glebowo-odpadowych (z terenu pozyskiwania węgla brunatnego i łupek bitumicznych). Na podstawie przeprowadzonych badań oznaczono poszczególne pule baru występujące w różnych frakcjach – jonowymiennej, węglanowej, zredukowanej, organicznej oraz pozostałej. W procedurach badawczych wykorzystano do ekstrakcji sekwencyjnej metodykę Tessiera.

Słowa kluczowe: bar, formy specjacyjne baru w glebach i odpadach, ekstrakcja sekwencyjna

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FUNGAL DISEASES ON THE REED-BED VEGETATION OF THE EUTROPHIC WASOSZE LAKE

CHOROBY GRZYBOWE ROŚLINNOŚCI SZUWAROWEJ EUTROFICZNEGO JEZIORA WĄSOSZE

Abstract: In 2006–2008 occurrence of pathogenic fungi on the reed-bed vegetation of the eutrophic Wasosze lake (West Pomerania, Drawsko district, Zlocieniec subdistrict) was examined. A total of 68 species of fungi colonizing 40 species of reed-bed plants and growing in the littoral zone of the lake were identified. The greatest number of taxa (24) belonged to the Ascomycetes, constituting 35 % of all fungal species collected. A slightly smaller number of species (22) were represented by anamorphic fungi (32 %). Basidiomycetes were represented by 19 taxa (28 %). Only three fungi-like organisms belonging to *Peronosporales* (5 %) were recorded (*Bremia lactucae*, *Peronospora myosotidis* and *P. ranunculi*). Three fungal species that are hyperparasites of parasitic fungi were recorded in the plant material: *Ampelomyces quisqualis*, *Ramularia uredinis* and *Sphaerellopsis filum*.

Keywords: parasitic fungi, eutrophic lake, Wasosze, *Sphaerellopsis*, *Ramularia*, *Peronospora*, *Erysiphe*, *Puccinia*, *Septoria*, *Septoriella*, *Leptosphaeria*

The Wasosze lake is located in the West Pomerania province, Drawsko district and Zlocieniec subdistrict. It is a long, narrow and relatively shallow (mean depth 3.5 m, maximum depth 8.5 m) water body with a total area of 326.4 ha. The coast line is not varied and the lake bottom is quite level with small local depressions. The lake basin is constricted and divided into northern and southern parts. The Wasawa river, the primary tributary of the Drawa river, flows through the lake. The waters of the Wasosze lake are rich in oxygen and nutrient mineral substances (phosphorus, nitrogen). Such conditions are favourable for the development of plankton and other forms of aquatic life, especially in the summer, and inhibit mineralization processes. This leads to water body ageing and dying of living organisms (*eg* fish) as well as slime accumulation [1–2]. An improvement in the quality of lake waters, biogenic compound concentration and

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phytoplankton abundance has been observed in the last few years. An increase in water transparency and oxygenation has not been recorded.

The Wasosze lake is an indirect receiver of wastewater from the village treatment plant in Wierzchowo. Local pollution from the northern region which covers the Bobrowo village also influences the water quality of the lake. The lake is no longer intensively exploited by the tourist industry [3]. The vegetation is uniform in eutrophic lakes and usually consists of *Phragmites australis*, *Schoenoplectus lacustris*, *Typha angustifolia* and *T. latifolia*. In shoaled areas, *Schoenoplectus lacustris* is replaced by sedge vegetation (tall sedges): *Carex acutiformis*, *C. acuta*, *C. rostrata*, *C. vesicaria*, which border on willow scrub and alder forests at the lake shore [4]. Despite recent studies, the knowledge on parasitic fungi on reed-bed plants both in Poland and worldwide is relatively poor [5–23]. The aim of this study was to identify species of pathogenic fungi occurring on reed-bed plants of the eutrophic Wasosze lake.

Material and methods

Overground parts (leaves, stems, inflorescence) of reed-bed plants growing in the littoral zone of the Wasosze lake exhibiting symptoms of colonization by parasitic fungi were examined. Plants were sampled once a month from May to November between 2006 and 2008. The floristic material was determined in the laboratory [24] and the species composition of parasitic fungi occurring in the material was identified.

Parasitic fungi caused pathological symptoms (*eg* different types of leaf spot diseases and necrosis) and aetiological symptoms (*eg* white coating and rusty pustules) on overground organs of the plants. Fragments of plants with pathological changes were cut with a razor blade under a stereoscopic microscope to identify pathogens. Plant fragments were mounted in a drop of diluted lactic acid and observed under a light microscope. Observations were usually conducted after three days as lactic acid clears the structures of the fungi and host tissue. Fungi were identified using morphological features of uninfected fruitbodies or cut plant fragments with fruitbody elements [25–31]. The nomenclature of fungi and fungi-like organisms was accepted after Mulenko et al [32].

Results and discussion

Preliminary results of investigations on parasitic fungi were discussed in the study "Grzyby pasożytnicze roślinności szuwarowej eutroficznego jeziora Wąsosze" [8]. However, only the results on fungi colonizing 13 selected plant species of the genera *Carex*, *Juncus*, *Phragmites* and *Typha* were reported. They are expanded in this work and supplemented with the data on all the other plant species collected together with parasitic fungi colonising them. Forty species of reed-bed plants growing in the littoral zone of the Wasosze lake were selected for the study: *Acorus calamus*, *Alnus glutinosa*, *A. incana*, *Caltha palustris*, *Calamagrostis arundinacea*, *Carex acuta*, *C. acutiformis*, *C. rostrata*, *C. vesicaria*, *C. vulpina*, *Chrysosplenium alternifolium*, *Crepis paludosa*, *Eleocharis palustris*, *Epilobium hirsutum*, *E. pariflorum*, *Glyceria maxima*, *Iris pseudo-*

acorus, *Juncus articulatus*, *J. bufonius*, *J. compressus*, *J. effusus*, *J. inflexus*, *Lysimachia vulgaris*, *Lythrum salicaria*, *Mentha aquaitca*, *Myosotis palustris*, *Oenanthe aquatica*, *Phalaris arundinacea*, *Phragmites australis*, *Ranunculus repens*, *Rumex hydrolapathum*, *Sagittaria sagittifolia*, *Salix fragilis*, *Schoenoplectus lacustris*, *Sium latifolium*, *Sparganium emersum*, *S. erectum*, *Stachys palustris*, *Typha angustifolia*, *T. latifolia*. A total of 68 fungal taxa were identified. These were plant pathogens traditionally considered to be fungi. *Peronosporales*, which were excluded from the kingdom *Fungi*, were the only exception. Pathogens of the genus *Peronosporales* were classified in the kingdom *Chromista* and were labelled as fungi-like organisms [33]. All fungi occurring on living organs of plants or on the mycelium of parasitic fungi were considered to be parasites in this study although they may belong to three ecological groups of parasites (obligate parasites, facultative saprotrophs, facultative parasites) based on the interaction with the host organism [34–35].

The greatest number of taxa (24) belonged to the Ascomycetes, constituting 35 % of all fungal species collected. A slightly smaller number of species (22) were represented by anamorphic fungi (32 %). Basidiomycetes were represented by 19 taxa (28 %). Only three fungi-like organisms belonging to *Peronosporales* (5 %) were recorded.

Fungi-like organisms: *Bremia lactucae*, *Peronospora myosotidis*, *P. ranunculi*.

Fungi-like organisms caused numerous, small, yellowish spots on the upper leaf surface of host plants (*Crepis paludosa*, *Myosotis palustris*, *Ranunculus repens*). A fine coating of sporangia and sporangiophores formed on the lower leaf surface at the site of the spots. Despite excellent environmental conditions (high humidity) favourable for their occurrence, *Peronosporales* constituted the smallest percentage of the pathogens recorded in the study (three species, 5 %). As reported in the literature, fungi-like organisms occur relatively frequently. However, pathological symptoms caused by them are difficult to notice as plants that are infected systemically, usually occur at the beginning of the vegetative season and are easy to spot. They are usually deformed, lighter in colour than healthy individuals due to a mass formation of sporangiophores on all parts of systematically infected plants, making them visible from a distance, or only on lower leaf surfaces. Later infections are usually local (for instance only leaves or other overground plant organs are infected) and their symptoms are usually difficult to notice [27, 36–37].

Ascomycetes: *Blumeria graminis*, *Claviceps microcephala*, *Epichloë typhina*, *Erysiphe aquilegiae* var. *aquilegiae*, *E. aquilegiae* var. *ranunculi*, *E. biocellata*, *E. cynoglossi*, *E. galeopsidis*, *E. heraclei*, *E. lythri*, *E. polygoni*, *Leptosphaeria caricina*, *L. culmifraga*, *L. sparganii*, *Metasphaeria cumana*, *Phaeosphaeria caricis*, *P. culmorum*, *P. eustoma*, *P. juncina*, *P. typharum*, *Paraphaeosphaeria michotii*, *P. vectis*, *Phyllachora junci*, *Sphaerotheca epilobii*.

Ascomycetes were diagnosed from 26 host plant species: *Acorus calamus*, *Caltha palustris*, *Calamagrostis arundinacea*, *Carex acuta*, *C. acutiformis*, *C. rostrata*, *C. vesicaria*, *C. vulpina*, *Epilobium pariflorum*, *Glyceria maxima*, *Iris pseudoacorus*, *Juncus effusus*, *Lythrum salicaria*, *Mentha aquaitca*, *Myosotis palustris*, *Oenanthe aquatica*, *Phalaris arundinacea*, *Phragmites australis Ranunculus repens*, *Rumex* *hydrolapathum*, *Schoenoplectus lacustris*, *Sium latifolium*, *Sparganium emersum*, *Stachys palustris*, *Typha angustifolia*, *T. latifolia*

As many as ten species of the 24 ascomycetes collected were causal agents of powdery mildew (*Blumeria graminis*, *Erysiphe aquilegiae* var. *aquilegiae*, *E. aquilegiae* var. *ranunculi*, *E. biocellata*, *E. cynoglossi*, *E. galeopsidis*, *E. heraclei*, *E. lythri*, *E. polygoni*, *Sphaerotheca epilobii*). The fungi formed a distinctive, white coating of the mycelium and conidial germination on overground plant parts. Causal agents of powdery mildew had a high tolerance to habitat conditions. They preferred moderate temperature and precipitation. They also infected plants during droughts as fungal spores contained a considerable amount of water (55–75 %) and could germinate without a drop of water. Spores of most pathogenic fungi germinate only in a drop of water as water content in their spores rarely exceeds 20 % [38]. Other ascomycete species formed highly numerous, small black spots on overground plant parts (mostly on stems and leaves). *Epichloë typhina* and *Claviceps microcephala* were the only exceptions. The former developed a yellowish-orange coating on culms of *Calamagrostis arundinacea* while the latter was recorded in reed inflorescences where it formed small sclerotia. Other species formed globose fruitbodies such as perithecia (*Epichloë typina* and *Phyllachora junci*) or pseudothecia (*Leptosphaeria caricina*, *L. culmifraga*, *L. sparganii*, *Metasphaeria cumana*, *Phaeosphaeria caricis*, *P. culmorum*, *P. eustoma*, *P. juncina*, *P. typharum*, *Paraphaeosphaeria michotii*, *P. vectis*) in pathological tissue fragments.

Basidiomycetes: *Melampsora epitea*, *Melampsoridium betulinum*, *Puccinia calthae*, *P. caricina* var. *caricina*, *P. chrysosplenii*, *P. coronata*, *P. dioicae* var. *dioicae*, *P. iridis*, *P. limosae P. magnusiana*, *P. menthae*, *P. scirpi*, *Pucciniastrum epilobii*, *Tolyposporium junci*, *Urocystis ranunculi*, *Uromyces rumicis*, *Ustilago filiformis*, *U. grandis*, *U. striiformis*.

Basidiomycetes were represented by 19 fungal species (28 % of all species). They were collected from 20 host plant species: *Alnus glutinosa*, *A. incana*, *Caltha palustris*, *Carex acuta*, *C. acutiformis*, *C. vesicaria*, *Chrysosplenium alternifolium*, *Epilobium hirsutum*, *Glyceria maxima*, *Iris pseudoacorus*, *Juncus bufonius*, *Lysimachia vulgaris*, *Lythrum salicaria*, *Mentha aquaitca*, *Phalaris arundinacea*, *Phragmites australis*, *Ranunculus repens*, *Rumex hydrolapathum*, *Salix fragilis*, *Schoenoplectus lacustris*. Rusts dominated and were represented by 14 species (*Melampsora epitea*, *Melampsoridium betulinum*, *Puccinia calthae*, *P. caricina* var. *caricina*, *P. chrysosplenii*, *P. coronata*, *P. dioicae* var. *dioicae*, *P. iridis*, *P. limosae P. magnusiana*, *P. menthae*, *P. scirpi*, *Pucciniastrum epilobii*, *Uromyces rumicis*). They formed elongated, light-brown pulverulent uredinia on the lower leaf surface. Elongated, fine, black thelia developed on the lower leaf surface slightly later. Smuts represented five species (*Tolyposporium junci*, *Urocystis ranunculi*, *Ustilago filiformis*, *U. grandis*, *U. striiformis*). They caused the formation of black agglutinated (*T. junci*) or pulverulent (*U. grandis*) spore masses at the infection site. Only *Tolyposporium junci* was recorded in the inflorescences of the plants. Other species were observed on culms and leaves. Smut infections can cause considerable plant underdevelopment and deformation, and can inhibit plant growth [10, 21, 28, 31, 36].

Anamorphic fungi: *Ampelomyces quisqualis*, *Asteroma alnetum*, *Cladosporium* spp., *Marssonina betulae*, *Mascostroma innumerosum*, *Passalora montana*, *Phyllosticta caricis*, *Ramularia calthae*, *R. didyma*, *R. lysimachiae*, *R. rumicis*, *R. uredinis*, *Septoria caricis*, *S. epilobii*, *S. lysimachiae*, *Stagonospora elegans*, *S. junciseda*, *S. paludosa*, *Septoriella junci*, *Sphaerellopsis filum*, *Stagonospora caricis*, *Tubercularia vulgaris*.

Anamorphic fungi were represented by 22 species, which constituted 32 % of all fungi. They were recorded on 18 host plant species: *Alnus glutinosa*, *A. incana*, *Caltha palustris*, *Carex vesicaria*, *C. vulpina*, *Eleocharis palustris*, *Epilobium hirsutum*, *E. pariflorum*, *Juncus articulatus*, *J. bufonius*, *J. compressus*, *J. inflexus*, *Lysimachia vulgaris*, *Mentha aquaitca*, *Phragmites australis*, *Ranunculus repens*, *Rumex hydrolapathum*, *Salix fragilis*, *Sparganium erectum*,

Anamorphic fungi formed either numerous and fine black spots with conidiomata embedded in the tissue (acervulus or picnidium) or a coating consisting of conidiophores and conidiospores [25–26, 39] on overground parts of the plants. Only *Tubercularia vulgaris* on dying and wooded organs of *Alnus incana* developed orange mycelium masses with sporodiocha. A mass production of conidiospores inside spordiocha was observed. A mass release of conidiospores was recorded especially in humid weather [40–41]. Three fungal species that are hyperparasites of parasitic fungi were recorded in the plant material: *Ampelomyces quisqualis*, *Ramularia uredinis* and *Sphaerellopsis filum*. Hyperparasites can limit the occurrence of their hosts by colonising and destroying the mycelium, oidia, uredinia and aecia of pathogens. A frequent occurrence of hyperparasites was observed in the studies on the presence of parasitic fungi on reed-bed plants. As literature data show, some hyperparasites of Uredinales can reduce rusts by up to 98 % in experimental conditions [7, 42–46].

Conclusions

Reed beds play an important role as natural filters in the process of self-purification of water, especially from pollution such as fertilizers or plant protection agents arriving from adjacent fields. Pathogenic fungi can contribute to the weakening and dying of the reed-bed vegetation. Some fungal species, so called hyperparasites, can naturally reduce plant pathogens and contribute to an improvement in the developmental condition of reed-bed plants.

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CHOROBY GRZYBOWE ROŚLINNOŚCI SZUWAROWEJ EUTROFICZNEGO JEZIORA WĄSOSZE

Zakład Ochrony Roślin
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Abstrakt: W latach 2006–2008 przeprowadzono badania nad występowaniem gatunków grzybów chorobotwórczych na roślinności szuwarowej jeziora eutroficznego Wąsosze (Zachodniopomorskie, gmina Drawsko, leśnictwo Złocieniec). Łącznie zidentyfikowano 68 gatunków grzybów zasiedlających 40 gatunków roślin występujących w strefie przybrzeżnej jeziora. Największa liczba taksonów (24) należała do Ascomycetes stanowiących 35 % wszystkich zidentyfikowanych grzybów. Niewiele mniejszą grupę stanowiły grzyby anamorficzne reprezentowane przez 22 gatunki (32 %). Basidiomycetes reprezentowało 19 taksonów (28 %). W trakcie badań stwierdzono obecność tylko organizmów należących do *Peronosporales* (*Bremia lactucae*, *Peronospora myosotidis* i *P. ranunculi*). Trzy gatunki grzybów reprezentowały grupę nadpasożytów: *Ampelomyces quisqualis*, *Ramularia uredinis* i *Sphaerellopsis filum*.

Słowa kluczowe: grzyby pasożytnicze, jezioro eutroficzne, Wąsosze, *Sphaerellopsis*, *Ramularia*, *Peronospora*, *Erysiphe*, *Puccinia*, *Septoria*, *Septoriella*, *Leptosphaeria*

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ECOLOGICAL METHODS OF BIRD CONTROL IN URBAN AGROCOENOSES IN WARSAW

PROEKOLOGICZNE METODY ZWALCZANIA PTAKÓW W AGROCENOZACH MIEJSKICH NA PRZYKŁADZIE WARSZAWY

Abstract: The development of city agglomeration and suburban areas largely affect animal, mainly bird, behaviour. Warsaw as an example of devastated landscape with developing industry and housing and degraded natural ecosystems creates excellent conditions for the invasion and settlement of bird populations. Increasing problem of overpopulated avifauna results in the dispersion of animal-borne diseases. This paper is focussed on the importance of avifauna for a city, on diseases birds might disperse and on ecological methods of bird control in public places like supermarkets and facades of historical buildings.

Keywords: city agglomeration, avifauna, animal-borne diseases

Migration of wild animals to city agglomerations has become a problem of increasing importance recently. One of the reasons is the rapid development of towns and their suburbia. Another problem lies in the development of monocultures and decline of natural forests or mid-field woodlands [1, 2]. All these factors combined result in changes of animal behaviour which demonstrate themselves in distinct

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ethopathologies like changes in food preferences. Birds living in towns willingly select boiled or baked food products. Another problem is in that animals have developed a taste for unique city welfare. This, however, is not good for animals since they have to compete for space with people and with other animals from neighbouring regions [3, 4]. This competition changed their behaviour compared with that typical for birds living wild. Ways of competition are being changed, hierarchy is being disturbed and birds become more aggressive towards representatives of their own species. During the last several years 247 species were noted in Warsaw. Out of this number 187 species occurred regularly and 60 were present occasionally or rarely. 131 species were regular breeders in the city area and 20 species were wintering there. Mean bird density in Warsaw during the breeding period is estimated at 300–700 pairs/km^2 [5–7]. The highest concentration of avifauna is observed in Warsaw city centre of an area of 52 km^2 where the density ranges from 830 to 1590 pairs/km^2. In winter the density reaches 2500–4500 ind./km^2 [6, 7].

Pigeons and house sparrows are the dominants which together constitute 2/3 of the whole breeding avifauna (3/4 in winter together with the rook). Subdominants of a lesser density are swifts, jackdaws, starlings, collared daws, magpies and tits (the blue tit and the great tit). In the autumn water bodies of the city are visited by mallards and black-headed gulls.

Threats to and protection of birds in the city centre

Central area of Warsaw provides some advantages to birds (food abundance, favourable breeding places in buildings, warm water in winter) but also poses some serious threats. Sky-scrapers, particularly glazed office blocks, or load-bearing steel cables of the Swietokrzyski Bridge are a problem to flying birds which may smash against such obstacles and eventually die. Development and new investments cause shrinking of the city green. Intensive care of the latter impoverishes food base, breeding places and refuges for birds. Collisions with running cars increase mortality in young birds. Drying water holes and ponds in parks hampers the access to water for mallards and their young. Steep concrete slopes of water bodies become an „ecological trap” which makes drinking or bathing impossible. Nests are being destroyed in the breeding period when it coincides with renovation of house elevations. This problem is responsible for the declining density of nesting falcons, kestrels, sparrows, swifts, starlings and pigeons.

A serious ecological problem of the town is also an excessive multiplication of domestic and stray cats hunting for young birds and destroying their nests when let free on the green around houses.

Nature Protection Act of 1991 [8] helped city avifauna by protecting birds in the central area of Warsaw. It is not allowed to kill, catch, scare and keep birds in captivity. It is possible to install nesting boxes in town greenery to help moving birds from house elevations. Another problem is associated with feeding birds in special places. Fodder should be similar to the natural bird’s food like eg sunflower or cereal seeds.

Birds as a source of infection

Warsaw is „besieged" by birds which means favourable conditions for spreading animal-borne diseases. These diseases are dangerous for human health and life. The harmfulness of birds is always associated with their passages, feeding grounds, nesting and lodging places. Its size depends largely on bird density in a given area. Dominating species (pigeon in Warsaw) are the main sources of threats and damages [9].

Birds soil and pollute surfaces they sit on. The amount of excreted faeces depends on the structure of alimentary tract. Consumption of processed food shortens the digestion period and increases the amount of excreta. After drying bird faeces may be ground and spread in a form of fine dust particles. Moreover, birds leave feathers and down. Population of species dominating in Warsaw are the source of endo- and egzoparasites, they also transmit rickettsias, viruses, fungi and bacteria. Bird faeces contain condensed allergens, eggs of parasites or fungal spores [10–12].

Birds entering buildings, shops, supermarkets and storehouses (particularly with food products) have recently become a problem. The main representative of such birds is the house sparrow which adjusted its behaviour to the functioning of these objects.

Methods of bird frightening

Control of sanitary pests posing a risk in food production and storage is legally regulated by the Directive 93/43/ECC of 10.06.93 which requires having the HACCP system [13, 14]. The system consists in limiting to a necessary minimum chemical measures in favour of preventive actions. Applied methods of inspection should enable detection and liquidation of plagues (including bird's ones) in the time the risk arises [15].

To limit bird populations one has to prevent them from nesting and lodging. Environmental friendly methods include various scaring methods: physical (nets,

Photo 1. Protecting nets on cornices of the SGGW building

spikes), chemical (liquid, gel taste applicators), acoustic (sounds) and visual (silhouettes of natural enemies, lamps) signals and natural enemies (falconry).

Specially designed barriers and physical obstacles are often used to hamper the access of birds to a given space. Polyethylene nets protecting large surfaces are most often used for this purpose. Another method is to install spikes on window sills or fences. The spikes are efficient in preventing birds from sitting and nesting (Photo 1).

Large shops and supermarkets often use acoustic frighteners which affect the sense of hearing by emitting ultrasounds heard by birds but not by humans. These devices are imported since they are not produced in Poland. They are very efficient in controlling bird density in apartments, shops and warehouses.

Silhouettes of attacking birds of prey that resemble predator's shadow are being glued on special screens along fast roads. Such figures frighten crows(*Corvus corone*), pigeons(*Columba sp*.) and other birds and prevent from accidental road collisions.

Conclusions

Birds in a common conviction are not harmful to man but under specific conditions of town agrocoenoses the situation is quite opposite. Possibilities of controlling undesired bird presence in towns are limited in our country due to a lack of specific environmental friendly repellents which might be helpful in the case of risk. Most products are available abroad but in Poland local production is missing. Due to increasing demand, professional repellents are imported, sold or lent by special firms.

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PROEKOLOGICZNE METODY ZWALCZANIA PTAKÓW W AGROCENOZACH MIEJSKICH NA PRZYKŁADZIE WARSZAWY

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Abstrakt: Rozwój aglomeracji i urbanizacja terenów podmiejskich wpływa w znaczący sposób na zmianę zachowań zwierząt, przede wszystkim ptaków. Warszawa jako przykład krajobrazu zdewastowanego, gdzie rozwija się przemysł oraz zabudowa, a naturalne ekosystemy ulegają degradacji stwarza świetne warunki do wprowadzania się i zasiedlania przez ptaki. W konsekwencji wzrasta problem nadmiernego zagęszczenia awifauny, a konsekwencji wpływa to na rozprowadzanie i emisje źródeł chorób od zwierzęcych. W pracy tej skupiono się na przedstawieniu znaczenia awifauny dla miasta, chorób jakie mogą roznosić oraz metod ekologicznego usuwania nadmiaru ptaków z miejsc publicznych np.: supermarketów, fasad zabytkowych budynków.

Słowa kluczowe: aglomeracja miejska, awifauna, choroby od zwierzęce

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INFLUENCE OF NATURAL ORGANIC MATTER ON FOULING AND ULTRAFILTRATION MEMBRANES PROPERTIES – AFM ANALYSIS

WPŁYW NATURALNYCH SUBSTANCJI ORGANICZNYCH NA FOULING ORAZ WŁAŚCIWOŚCI MEMBRAN ULTRAFILTRACYJNYCH – ANALIZA AFM

Abstract: Low pressure membrane processes *ie* microfiltration and ultrafiltration are widely applied in water and wastewater treatment. The main exploitation problem connected with those technologies is the decrease of membrane capacity during the process caused by blocking of membrane pores with organic and inorganic substance (so-called fouling). The performance of atomic force microscopy analysis enables quantitative determination of membranes roughness and allows to characterize membrane surface before and after fouling. The paper discuss results of filtration of three surface waters differ in properties, mainly in specific UV absorbance ($SUVA_{254}$).

Keywords: fouling, ultrafiltration, natural organic matter, atomic force microscopy

Ultrafiltration is one of the low pressure membrane techniques applied in drinking water production. The method allows to remove colloids and high molecular weight substances from treated medium. However, a decrease of the permeate flux during the membrane filtration is one of the most important operating problems. *Natural Organic Matter* (NOM) interacts with membrane surface and pores and induces its fouling [1]. Except for organic substances, the type of a membrane also has a significant influence on fouling extent. Both, adsorption properties connected with hydrophobicity and electrostatic repulsion forces resulted from membrane material and foulant charges are considered [2].

Specific UV absorption (SUVA) can be used as a parameter describing hydrophobicity or aromaticity of NOM present in water [3]. However, chemical parameters of

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water *ie* pH, ionic strength and concentration of calcium ions can affect SUVA value [4]. The low value of SUVA indicates the greater concentration of non-humic fraction of organic matter present in water. The high value of SUVA indicates the greater concentration of aromatic compounds [5, 6].

To determine the structure of a membrane various microscopic techniques are used [7, 8] *eg Scanning Electron Microscope* (SEM), *Transmission Electron Microscope* (TEM), *Field Emission Scanning Electron Microscopy* (FESEM) and *Atomic Force Microscopy* (AFM). By means of those techniques the actual picture of membrane morphology can be obtained. AFM technique gives the picture of non-conductive structures with the resolution of 1 nm in both, air or liquid environment. Moreover, the sample does not require drying, thus, it is not deformed as in case of TEM or SEM [8]. The performance of atomic force microscopy analysis enables quantitative determination of *membranes mean roughness* (R_a) and *mean square roughness* (R_q). It allows to characterize membrane surface before and after fouling occurrence. AFM analysis is performed using electrons beam and sharp tip. The sample of membrane does not need to be coated with any extra material, however the obtained data can be deformed according to differences between shapes of either pore or support tip of microscope probe [9].

The wettability with distilled water is the significant membrane parameter. Hydrophobicity/hydrophilicity can be described by the measurement of the contact angle between the water drop and the membrane surface [5]. It is stated that the membrane is highly hydrophilic if the contact angle equal to 0^o (complete wetting) and highly hydrophobic for the contact angle above 90^o (no wetting) [10, 11]. To sum up, the greater contact angle the more hydrophobic membrane.

The aim of the study was to determine the influence of NOM on both, ultrafiltration membranes properties and the intensity of fouling. The effect of NOM on the retention coefficients of organic contaminants was also investigated.

Materials and methods

Experiments were carried out in MilliporeCDS10 (Millipore&Amicon), dead-end type stirred UF cell, using a feed volume of 2000 cm^3. The process pressure was maintained at 0.1 MPa and temperature was 20 ^oC. The diameter of the membrane disc was 76 mm. The experiments were conducted using *polyether-sulphone* (Millipore) (PES), *polyacrylonitrile* (PAN), *polysulphone* (PS), *poly(vinylidene fluoride)* (PVDF) (KOCH Membrane Systems) and *cellulose acetate* (GE Osmonics Labstore) (CA) membranes. The nominal *molecular weight cut off* (MWCO) was 10, 20, 10, 30 and 20 kDa for PES, PAN, PS, PVDF and CA, respectively.

Measurements of contact angle were performed using the goniometer (Pocket Goniometer PG-1) and the sessile drop method was applied. The angle between drop of water, membrane surface and air was measured according to Yoon et al [12]. The obtained contact angles were 73.1 ± 5.0^o, 65.7 ± 4.5^o, 63 ± 2.4^o, 49.6 ± 4.9^o and 39.1 ± 5.0^o for PES, PAN, PS, PVDF and CA, respectively. This allowed to classify membrane materials as ranging between strongly hydrophobic and strongly hydrophilic.

CA membrane was found to be the most hydrophilic and PES membrane as the most hydrophobic.

Pictures of membranes surface were made using contact atomic force microscope. Membranes, after preliminary drying were placed on a metal plate which was next placed in the microscope. Pictures were registered for sectors of dimensions 50 × 50 μm and 5 × 5μm. The setpoint varied at ranges 5.725– –2.725, –4.65– –2.5, –2.475–0, –4.075– –3.050 and –3.875– –3.3V for CA, PVDF, PS, PAN and PES membranes, respectively. The scan rate was equal to 5.086 Hz for all membranes.

Prior to the first use, the membranes were conditioned according to the manufacture protocol using Milli-Q water. The new membrane was used for each filtration. Fluxes of distilled water J_m ($t = 20\ ^{o}C$) were 98.7–311.2, 52.4–81.0, 39.92–105.72, 44.6–70.71 and 32.7–39.6 $dm^3/m^2 \cdot h$ for PES, PAN, PS, PVDF and CA, respectively.

In the membrane filtration three different surface water samples were used. Zabie Doly – "Zabie D" ("Frog Ditches") is a nature and landscape protected area in the centre of the highly-urbanized region of Upper Silesia (Poland). Many centuries of human activity, in particular underground mining and metal smelting, left the area covered with unused water retention pools, post-mining sinkholes, tailings and slag heaps. The second water "Lasek S" was sampled from a lake located in the forest (Piasniki district in Swietochlowice, Upper Silesian Region). The third water sample "Las P" originated from a lake located in the forest in the town of Poraj (near City of Czestochowa, Poland). The lake is a hydrographic basin of the surrounding forest.

The concentration of NOM in the feed and permeate was measured as TOC (Total Organic Carbon), DOC (Dissolved Organic Carbon) and by UV absorbance at $\lambda = 254$ nm (UVA_{254}). TOC and DOC were measured using a TOC Analyzer (HiPerTOC), while UVA in an UV/VIS spectrophotometer (CECIL 1021). Prior to the UV and DOC measurements the samples were subsequently filtered with 0.45 μm cellulose filters (Sartorius Stedim Biotech S.A.). SUVA was calculated as the ratio of UVA to DOC. The conductivity and pH were measured using a Microcomputer pH/conductivity meter CPC-551. The pH, UVA, DOC and SUVA of natural waters are shown in Table 1.

Table 1

Feed water characteristics

Sample	pH	k [μS/cm]	DOC [mg/dm^3]	TOC [mg/dm^3]	UVA_{254} [1/cm]	SUVA [m^2/gC]
Zabie D	6.90 ± 0.02	907.7 ± 2,5	13.40 ± 0.22	13.40 ± 0.31	0.099 ± 0.000	0.74
Lasek S	6.96 ± 0.03	260.8 ± 2.5	10.65 ± 0.24	12.67 ± 0.07	0.240 ± 0.001	2.25
Las P	6.52 ± 0.03	82.6 ± 2.5	8.90 ± 0.24	18.10 ± 0.35	0.304 ± 0.002	3.43

Moreover, in order to measure the particulate fouling potential of feed waters for low pressure membranes, the *unified membrane fouling index* (UMFI) was determined. UMFI value can be assigned from the dependence between normalized membrane specific flux and unit permeate capacity, regardless of hydrodynamic process conditions [13, 14].

Results and discussion

In the present work five different UF membranes were tested. The water from Las P (SUVA values close to 4) indicated that NOM was dominated by high molecular weight, hydrophobic humic acid fractions. For water form Lasek S, SUVA ratio was in the range 2–4. Water of such qualities is normally dominated by a mixture of hydrophobic and hydrophilic fractions of different molecular weights, humic and fulvic acids. For raw waters with SUVA below 2 (Zabie D), NOM is normally dominated by mostly non-humic, low molecular weight substances of low hydrophobicity [3].

Table 2

Retention coefficients of TOC and DOC

Sample	ZABIE D					LAS S					LAS P				
Membrane	PES	PAN	PS	PVDF	CA	PES	PAN	PS	PVDF	CA	PES	PAN	PS	PVDF	CA
R_{TOC} [%]	7.79	22.95	10.99	9.00	12.51	37.43	27.53	37.18	32.68	26.04	58.92	48.02	58.37	64.30	45.98
R_{DOC} [%]	8.13	23.23	11.32	8.75	12.84	18.55	21.08	21.34	18.11	19.46	12.41	8.55	11.24	4.16	29.30

The highest retention of organic compounds was obtained for Las P water regardless the membrane applied, next for Las S water and the lowest for Zabie D water. It was probably caused by the highest difference between TOC and DOC concentration of Las P water (Table 1). The retentions of DOC did not exceed 30%. Similar values were obtained during filtration of Las S water (characterized with the most heterogenic composition) regardless the membrane used. Moreover, these were the greatest values of R_{DOC} obtained for particular membranes. The only exception was the retention of DOC obtained for Las P water during filtration with CA membrane. The highest value of retention coefficient was probably caused by the adsorption of positively charged particles on negatively charges membrane surface.

The main advantage of using UMFI over other fouling indices is its universality *ie* it is independent of filtration scale or mode [14]. Figure 1 depicts the values of UMFI for each filtration. In case of Zabie D and Las S waters the fouling of membranes follows the trends: PES > PS > PVDF > CA. This is in agreement with pervious consideration of Zularisam et al [13] for membrane–foulant interactions. The hydrophobic membranes (PES) tended to foul more than hydrophilic membrane (CA). It was ascribed to the electrostatic adsorption occurring between negatively charged functional group of NOM and the membrane (positively) charged polymer [15, 16] of hydrophobic membrane (PES, PAN). Natural organic matter present in Las P water caused the smallest fouling of intensity comparable for all membranes. It could result from a significant share of non-dissolved organic compounds, which deposited on the membrane and acted as a protective layer for membrane pores. The highest fouling was observed in all cases for Las S water. The SUVA value obtained for this water indicated the content of both aromatic and aliphatic substances, what confirmed the significant influence of foulant-foulant interaction on fouling.

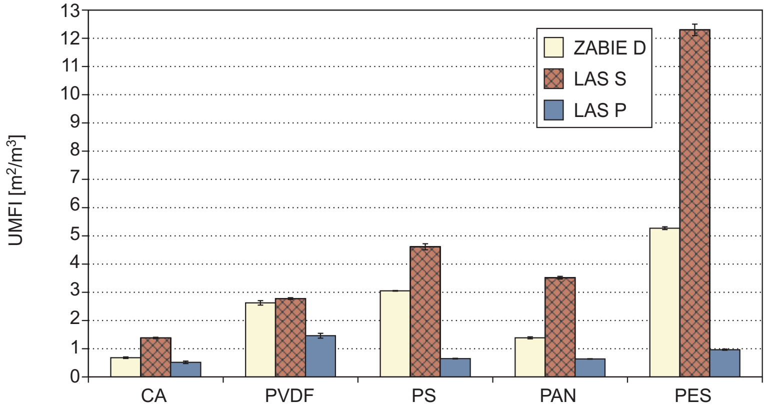

Fig. 1. Calculated UMFI indexes

Mean roughness (R_a) and *mean square roughness* (R_q) of clean and used membranes measured for both sectors *ie* a) 50 × 50 µm, b) 5 × 5 µm are shown in Fig. 2. The highest values of both, mean roughness and mean square roughness were obtained for PAN membrane. Its surface was the most diversified considering geometry, thus the smaller membrane sectors showed unrealistic pictures (Fig. 3). For this reason,

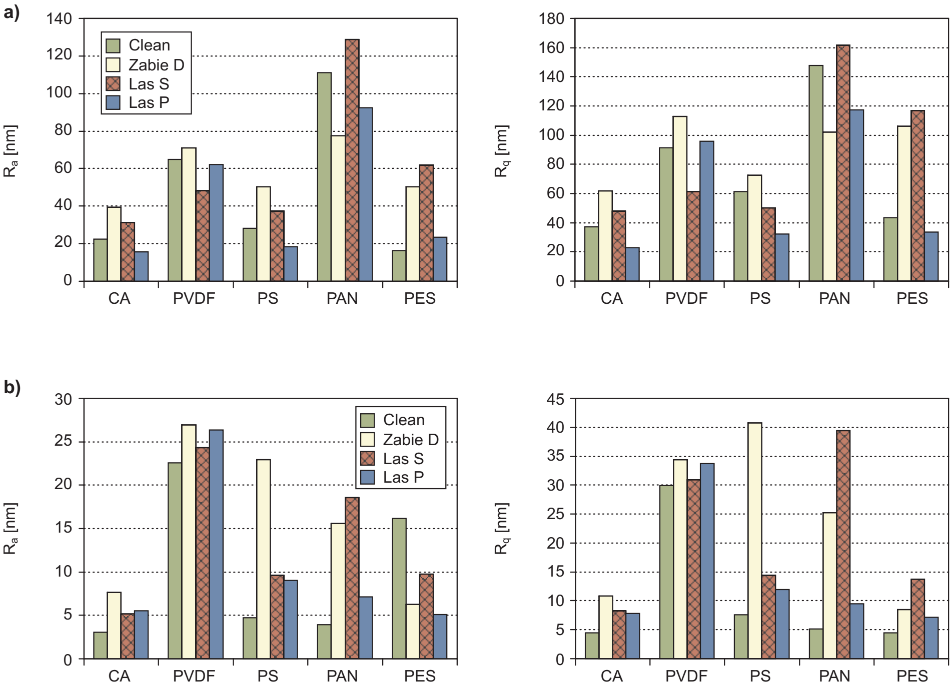

Fig. 2. R_a and R_q of new and used membranes: a) sector 50 × 50 µm, b) sector 5 × 5 µm

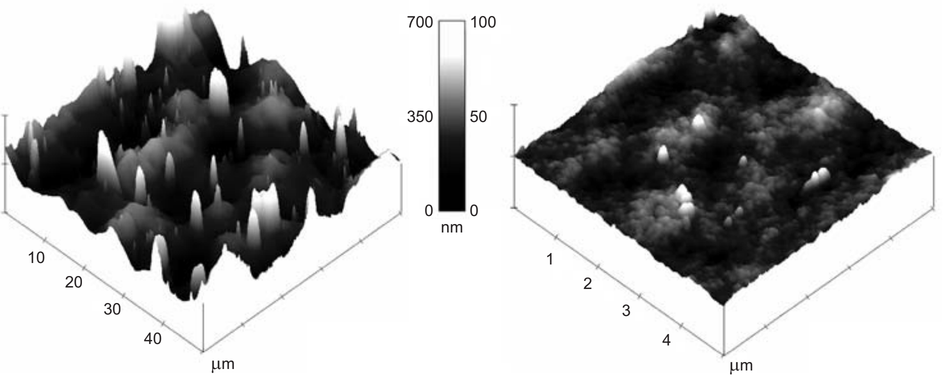

Fig. 3. The comparison of surface for different sectors of PAN membrane

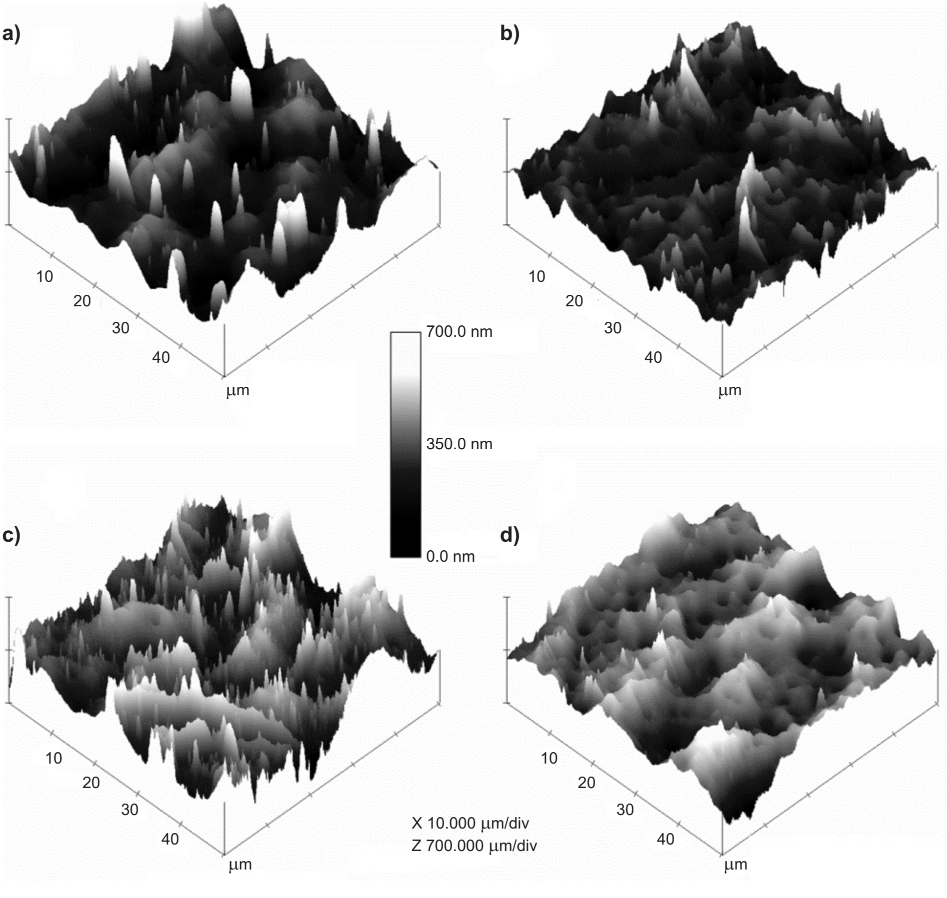

Fig. 4. The comparison of PAN membrane surface: a) clean membrane, b) after filtration of Zabie D water, c) after filtration of Las S water, d) after filtration of Las P water

membrane sectors of 50 × 50 μm were used for analysis. The smallest roughness was observed for PES membrane. However, irregularities sporadically appearing on its surface could have been seen.

The increase of both, mean roughness and mean square roughness was observed after filtration of Zabie D water for all membranes except for PAN membranes. Zabie D water characterized with high content of mineral substances (Table 1), which could partially crystallize on membranes surface increasing the roughness. In case of PAN membranes those compounds could penetrate its irregular surface and caused its smoothing. Moreover, non-aromatic organic compounds present in Zabie D water could also adsorb on membrane surface. The changes of PAN membrane surface are shown in Fig. 4.

The smoothing of membranes surface and the decrease of mean square porosity were observed after filtration of Las P water except for PES membrane. Non-dissolved organic compounds affected the irregularity of more rough membranes, on the other

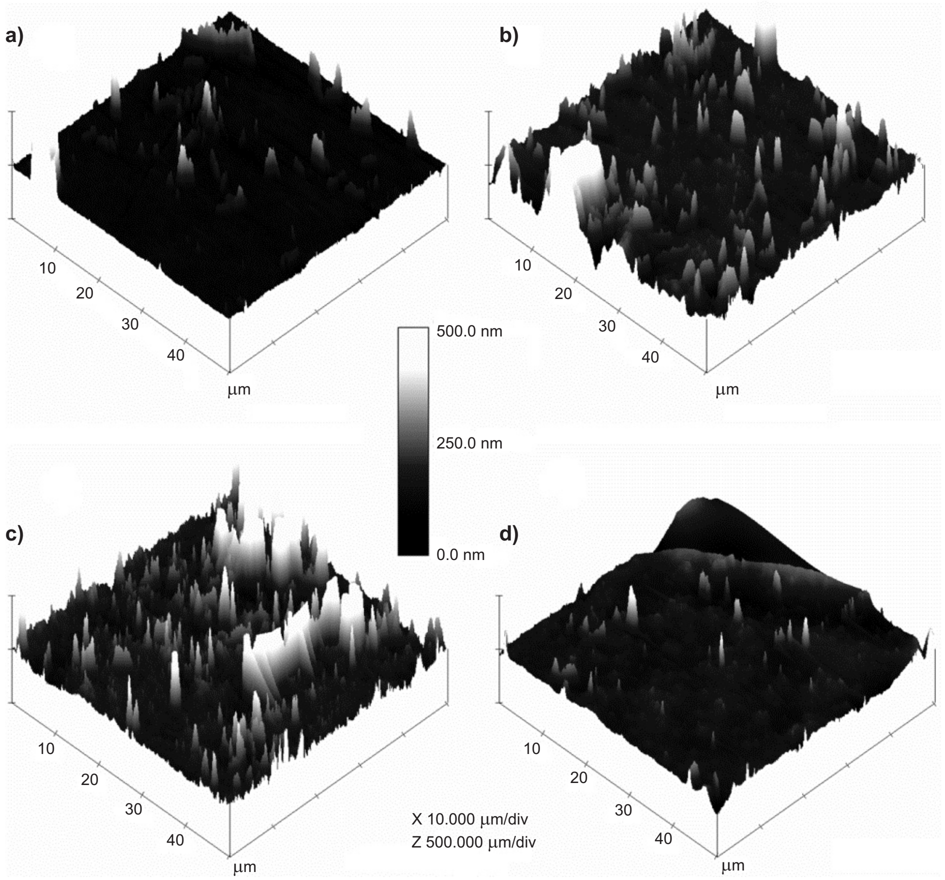

Fig. 5. The comparison of PES membrane surface: a) clean membrane, b) after filtration of Zabie D water, c) after filtration of Las S water, d) after filtration of Las P water

hand caused the roughness increase of the smoother membrane (PES), thus its surface became more uniform (lower R_q). The changes of PES membrane surface are shown in Fig. 5.

The filtration of Las S water resulted in the increase of R_a and R_q of CA, PAN and PES membranes. The changes of CA membrane surface are shown in Fig. 6. The increase of R_a was also observed for PS membranes, however its surface became more uniform than before the filtration (lower R_q). The surface of PVDF membrane became smoother and more uniform. The differences between changes in membranes surface can result from water heterogeneity.

Fouling affected also membranes wettability. The observed changes in contact angle values are shown in Fig. 7. The increase of hydrophobic character of membranes for which the initial contact angle was below 50° was stated regardless the water type. Opposite phenomenon was observed for membranes of contact angle above 63°.

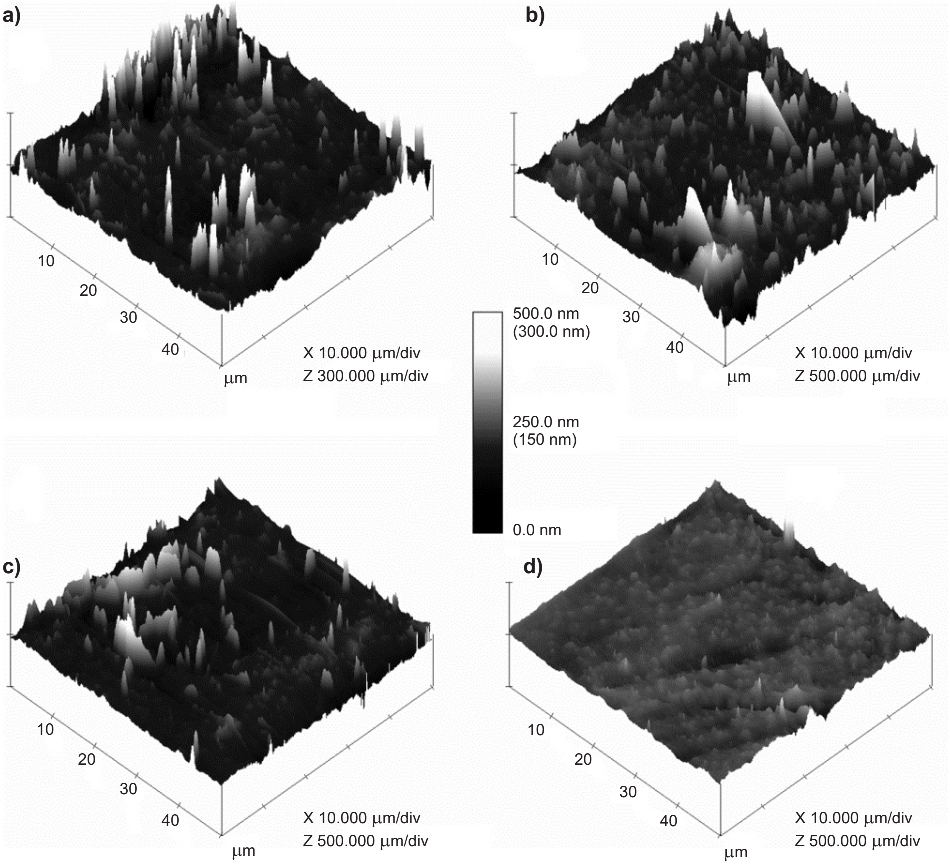

Fig. 6. The comparison of CA membrane surface: a) clean membrane, b) after filtration of Zabie D water, c) after filtration of Las S water, d) after filtration of Las P water

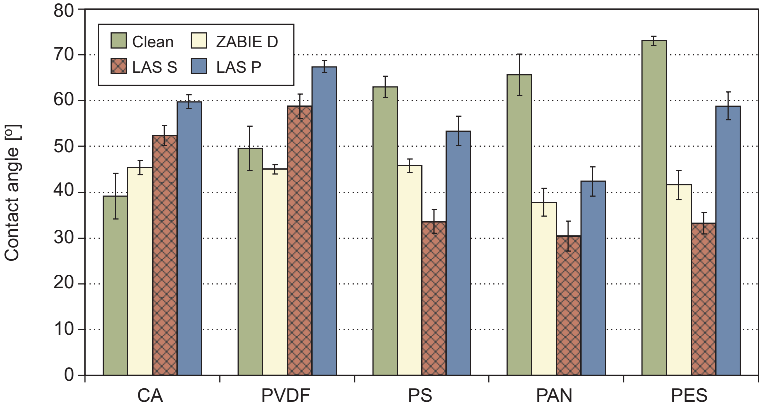

Fig. 7. Changes of contact angle of the new and used membranes

Conclusions

The mechanism of spherical exclusion is significant during TOC removal, while for DOC removal foulant-foulant interaction and adsorption on the membrane are of the greatest importance.

Hydrophobic membranes (*eg* PES) tends to foul more than hydrophilic ones (*eg* CA). Such a tendency is not observed for waters in which the difference between TOC and DOC content is high. Such waters caused smaller fouling as non-dissolved particles deposit on membrane surface forming a protective layer for membrane pores. The highest fouling is caused by water for which SUVA value indicates the presence of both aromatic and aliphatic substances, what confirmed the significant impact of foulant-foulant interactions on fouling.

Substances stopped on a membrane significantly affect its properties *ie* wettability and roughness. Depending on water and initial membrane properties the roughness can increase or decrease. Membranes of small roughness reveal the greatest ability to foul during filtration of low and medium SUVA value waters. In case of Las P water the difference between TOC and DOC content seems to be the more important property than the type of organic substance. This water causes the greatest fouling of membrane of high mean roughness and medium mean square roughness.

Acknowledgments

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WPŁYW NATURALNYCH SUBSTANCJI ORGANICZNYCH NA FOULING ORAZ WŁAŚCIWOŚCI MEMBRAN – ANALIZA AFM

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Abstrakt: Niskociśnieniowe techniki membranowe, ultrafiltracja i mikrofiltracja, stosowane są do oczyszczania i uzdatniania wody. Głównym problem eksploatacyjnym jest zmniejszanie wydajności membrany w trakcie procesu, związane z blokowaniem porów przez substancje organiczne i nieorganiczne (tzw. fouling). Analiza mikroskopem sił atomowych (AFM) umożliwia ilościowe określenie chropowatości powierzchni membrany, co pozwala scharakteryzować powierzchnię membran przed i po foulingu. W artykule przedstawiono wyniki filtracji trzech wód powierzchniowych różniących się głównie specyficzną absorbancją w nadfiolecie ($SUVA_{254}$).

Słowa kluczowe: fouling, ultrafiltracja, naturalne substancje organiczne, mikroskop sił atomowych

Indexes

CONTENTS OF VOLUME 19
OF "ECOLOGICAL CHEMISTRY AND ENGINEERING A"

SPIS TREŚCI TOMU 19
MIESIĘCZNIKA CHEMIA I INŻYNIERIA EKOLOGICZNA A"

Papers/Artykuły

1–2

3

4–5

6

7

8

9

10

11

12

AUTHOR INDEX OF VOLUME 19 OF "ECOLOGICAL CHEMISTRY AND ENGINEERING A"

WYKAZ AUTORÓW PUBLIKACJI ZAMIESZCZONYCH W TOMIE 19 MIESIĘCZNIKA „ECOLOGICAL CHEMISTRY AND ENGINEERING A / CHEMIA I INŻYNIERIA EKOLOGICZNA A"

Meaning of the digits in the index entries – (no. of issue) first page, *no. of the article* (in the volume contents).

Sposób zapisu odnośników haseł – (nr zeszytu) pierwsza strona artykułu, *nr artykułu* (w spisie treści rocznika).

SUBJECT INDEX

Meaning of the digits in the index entries – (no. of issue) first page, *no. of the article* (in the volume contents).

INDEKS RZECZOWY

Sposób zapisu odnośników haseł – (nr zeszytu) pierwsza strona artykułu, *nr artykułu* (w spisie treści rocznika).

INDEX OF LATIN, POLISH AND ENGLISH SPECIES NAMES OF MICROORGANISMS, PLANTS AND ANIMALS AND THEIR ANATOMICAL PARTS

WYKAZ ŁACIŃSKICH, POLSKICH I ANGIELSKICH NAZW MIKROORGANIZMÓW, ROŚLIN I ZWIERZĄT I ICH CZĘŚCI ANATOMICZNYCH

Meaning of the digits in the index entries – (no. of issue) first page, *no. of the article* (in the volume contents).

Sposób zapisu odnośników haseł – (nr zeszytu) pierwsza strona artykułu, *nr artykułu* (w spisie treści rocznika).

INDEX OF ACRONYMS

Meaning of the digits in the index entries – (no. of issue) first page, *no. of the article* (in the volume contents).

WYKAZ AKRONIMÓW

Sposób zapisu odnośników haseł – (nr zeszytu) pierwsza strona artykułu, *nr artykułu* (w spisie treści rocznika).

Varia

CENTRAL EUROPEAN CONFERENCE ECOpole ’12
Short Conference Report

The Conference ECOpole ’12 was held in 10–13 X 2012 at the Conference Center “Rzemieslnik” in Zakopane, PL. It was the twenty first ecological conference of the series of meetings organised by the Society of Ecological Chemistry and Engineering, Opole, PL.

148 participants, including delegates representing 8 countries (Austria, Czech Republic, Germany, Hungary, Poland, Romania, Russian Federation, Slovakia) took part in the event and presented 18 oral contributions and 144 posters.

The Abstracts of the Conference contributions were available on the Conference website before and during the Conference.

The Conference issue of the quarterly *Ecological Chemistry and Engineering S* 2012, **19**(3) containing among others keynote speakers papers, was distributed at the Conference Reception desk together with a CD-ROM (containing short info on Keynote Speakers, Abstracts of the Conference presentations as well as ECOpole’12 Conference Programme).

On Wednesday (10th October 2012) after short Opening Ceremony (prof. Maria Waclawek Chairperson of the Organising Committee and prof. Witold Waclawek, Chairman of the Conference Scientific Board and President of the Society of Ecological Chemistry and Engineering) at 19.00 the participants were invited for Musical Soirée realised by students of the Fryderyk Chopin State School of Music in Nowy Targ. The Programme contained works by F. Chopin, W.A. Mozart, R. Binge, C. Camilleri, R. Friml, A.L. Webber and K. Zeller. The audience applauded the players and claimed for encore.

At 20.15 started Get-Together Party.

The Conference Agenda was divided into 5 sections:
– SI Chemical Pollution of Natural Environment and its Monitoring
– SII Environment Friendly Production and Use of Energy
– SIII Risk, Crisis and Security Management
– SIV Forum of Young Scientists and Environmental Education
– SV Health, Ecology and Agriculture.

On Thursday, 11th October 2012 at 9.00 a.m. prof. **Marina V. FRONTASYEVA** (*Joint Institute for Nuclear Research, Dubna, RU*) initiated the First Plenary Session with the invited lecture: “Atmospheric deposition of trace elements in Europe – assessment based on moss analysis”. This contribution was met with great interest of the audience. During the conference the plenary lectures were also delivered by other invited lecturers: prof. **György HELTAI** and prof. **Agnes BALINT** (*Department of Chemistry and Biochemistry, Szent István University, Gödöllő, HU*): "Contribution of agricultural field production to emission of greenhouse gases (GHG)", prof. **Jacek WANKOWICZ** (I*nstitute of Power Engineering, R&D Centre, Warszawa, PL*): "Polish road map towards low carbon energy technologies", prof. **Roman ZARZYCKI** and doc. **Zofia MODRZEJEWSKA** (*Higher Vocational State School in Kalisz; Lodz University of Technology, Łódź, PL*): *"*Theory of kinetics of adsorption on hydrogel chitosan granules" prof. **Elena MASAROVICOVA** (*Comenius University, Bratislava, SK*): "Occurence, characterization and action of metal nanoparticles" and prof. **Manfred SAGER** (*Sonderuntersuchungen Elementanalytik, AGES Wien, AT*): "Composition of apples – differences due to varieties and cultivation methods".

There were also presented very interesting lectures, *eg*: S. **Franzle, R. Bertheau, and H. Heidenreich** (*IHI Zittau, DE*): "Chitin adsorption in natural conditions – spatial distribution and chances for biomonitoring", **J. Kriz, D. Jezbera, F. Studnicka** and **P. Seba** (*University of Hradec Kralove, Hradec Králové, CZ*): "Non-invasive continuous monitoring of heart rate", **M. Sprynskyy and B. Buszewski** (*Nicolaus Copernicus University, Toruń, PL*): "Removal of uranium ions from aqueous solutions by talc and diatomite: kinetic and equilibrium studies", **A. I. Stoica, N. C. Godja, J. Wosik, M. Polzler** and **Ch. Kleber** (*Centre of Electrochemical Surface Technology, Wiener Neustadt, AT*): "Corrosion protection of aluminium alloys by different types of silanes", **K.J. Nowak, A.T. Solecki** and **T.J. Szadej** (*University of Wroclaw, Wrocław, PL*): "Radiological risk connected with mining waste from spoil tips of the uraniferous coal, Okrzeszyn area (Sudetes) in the case of the landscape architecture application", **T. Rodziewicz, A. Zaremba** and **M. Waclawek** (*Opole University, Opole; Czestochowa University of Technology, Częstochowa, PL*): "Perspectives of photovoltaics".

Thursday, a day of hard work, was finished with the Poster Session of the Section Analytical Methods and Energy Production. Many of the discussions started at the posters, lasted until the evening hours.

At 19.30 the Conference participants were invited for a Conference Dinner.

As usually during the ECOpole Conferences, the second day included the Session of the Young Scientists (a forum of young scientists that present and discuss local ecological problems of their countries). During the Young Scientists', Environmental Education and Renewable Energy Poster Session 39 posters were presented.

The Scientific Board (**prof. Roman Zarzycki** (*Higher Vocational State School in Kalisz, Kalisz, PL*), **prof. Marina V. Frontasyeva** (*Joint Institute for Nuclear Research, Dubna, RU*), **prof. Manfred Sager** (*Sonderuntersuchungen Elementanalytik, AGES Wien, AT*), **prof. Bohumil Vybiral** (*University of Hradec Kralove, Hradec Králové, CZ*) and **prof. Witold Waclawek** (*Society of Ecological Chemistry and Engineering, Opole, PL*)) granted awards (sponsored by the Society of Ecological Chemistry and Engineering) for the best presentations. The award for oral presentations were given to: **Klara PIOTROWSKA, MSc** (*Lodz University of Technology, Łódź, PL*) for the lecture **K. Piotrowska, M. Imbierowicz** and **A. Chacuk**: "Wet oxidation of dairy sewage: the kinetic study of decomposition of the compounds included in the milk product – protein, fat, lactose, and intermediate products of decoposition”, **Dr Anca STOICA** (*Centre of Electrochemical Surface Technology, Wiener Neustadt, AT*) for the presentation **A. I. Stoica, N. C. Godja, J. Wosik, M. Polzler** and **Ch. Kleber**: “Corrosion protection of aluminium alloys by different types of silanes” and **Aleksandra ZIEMINSKA-STOLARSKA, Msc** (*Lodz University of Technology, Łodz, PL*) for oral presentation **A. Zieminska-Stolarska, A. Polanczyk, I. Zbicinski** and **J. Skrzypski**: “Analysis of the impact of changes in the flux of biogenic substances on water eutrophication in the Sulejow reservoir”.

The awards for poster presentations were given to **Jakub SKUT, Msc** (*Wroclaw University of Technology, Wrocław, PL*) for the poster: **J. Hoffmann, J. Skut** and **J. Zmuda**: “The content of selected phosphorus forms in PAPR-type fertilizers enriched with sulfur”, to **Katarzyna Maria JAROMIN, Msc** (*Lublin University of Technology, Lublin, PL*) for the poster: **K. M. Jaromin** and **G. Lagod**: “Efficiency of selected pollution removing from municipal wastewater in the laboratory bioreactor SBR type” and to **Matus PESKO, Msc** (*Comenius University, Bratislava, SK*) for the poster: **M. Pesko** and **K. Kralova**: “Physiological response of *Brassica napus* L. plants to Cu(II) treatment” and **Paweł KREMS, Msc** (*Opole University, Opole, PL*) for the poster: **M. Rajfur, P. Krems** and **A. Klos**: “Aquatic plants – a source of information about surface water pollution with heavy metals”.

Closing the conference, prof., prof. Maria and Witold Waclawek made short recapitulation. In general, ECOpole’12 was focused on monitoring of the quality of natural environment, its effects on human life, environmental education as well as application of renewable sources of energy.

They expressed gratitude to all participants for coming and taking active part in the Conference and thanked all Chairpersons of Sessions.

They announced, that full texts of the presented papers will be published (after obtaining reviewers’ positive opinions) in the successive issues of the journals *Ecological Chemistry and Engineering A* and *S* and they will be distributed to all participants.

The Extended Abstracts of the presentations will be published in two subsequent issues of semi-annual *Proceedings of the ECOpole*.

At the end they invited all Colleagues to attend the ECOpole’13 Conference, which will be held in Hotel **Ziemowit in Jarnoltowek**, PL in the next October.

On Saturday morning an excursion was organised to the Tatra National Park – the Education Center.

Professor Barbara KUDRYCKA, Minister of Science and Higher Education took the Honorary Patronage of the conference ECOpole’12 and became President of the Honorary Committee.

Maria Wacławek

INVITATION FOR
ECOpole ’13 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 22nd annual Central European Conference ECOpole ’13, which will be held in 23–26 X 2013 (Wednesday–Saturday) in Hotel Ziemowit in Jarnoltowek, PL.

The Conference Programme includes oral presentations and posters and will be divided into five sections:

- **SI Chemical Pollution of Natural Environment and Its Monitoring**
- **SII Environment Friendly Production and Use of Energy**
- **SIII Risk, Crisis and Security Management**
- **SIV Forum of Young Scientists and Environmental Education in Chemistry**
- **SV Impact of Environment Pollution on Food and Human Health**

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format),
- extended Abstracts (5–8 pages) in the semi-annual journal *Proceedings of ECOpole*,
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

The deadline for sending the Abstracts is **15th July 2013** and for the Extended Abstracts: **1st October 2013**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2013**) on the Conference website:

ecopole.uni.opole.pl

The papers must be prepared according to the Guide for Authors on Submission of Manuscripts to the Journals.

At the Reception Desk each participant will obtain abstracts of the Conference contributions as well as the Conference Programme recorded on electronic media (the Programme will be also published on the ECOpole ’13 website).

After the ECOpole ’13 Conference it will be possible to publish electronic version of presented contributions (oral presentations as well as posters) on the website.

Further information is available from:
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ECO OPOLE'13

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

w dniach 23-26 X 2013, w Hotelu Ziemowit w Jarnółtówku

Będzie to **dwudziesta druga z rzędu** konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole ’13 będą zgrupowane w pięciu Sekcjach:

- **Chemiczne substancje w środowisku przyrodniczym oraz ich monitoring**
- **SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie**
- **SIII Zarządzanie środowiskiem w warunkach kryzysowych**
- **SIV Forum Młodych (FM) i Edukacja prośrodowiskowa**
- **SV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi**

Materiały konferencyjne będą opublikowane w postaci:

- abstraktów (0,5 strony formatu A4) na CD-ROM-ie,
- rozszerzonych streszczeń o objętości 5–8 stron w półroczniku *Proceedings of ECOpole,*
- artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering*/ *Chemia i Inżynieria Ekologiczna* (*Ecol. Chem. Eng.*) ser. A i S oraz w półroczniku *Chemistry – Didactics – Ecology – Metrology* (*Chemia – Dydaktyka – Ekologia – Metrologia*).

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tchie.uni.opole.pl

Po konferencji zostaną wydane 5–8-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te winny być przesłane do **1 października 2013 r.** Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej.

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Po konferencji będzie możliwość opublikowania elektronicznej wersji prezentowanego wystąpienia (wykładu, a także posteru) na tej stronie.

Prof. dr hab. inż. Maria Wacławek
Przewodnicząca Komitetu Organizacyjnego
Konferencji ECOpole '13

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[7] Simeonov D, Spasov L, Simeonova P. Statistical calibration of model solution of analytes. Ecol Chem Eng A. Forthcoming 2012.

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