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CONTENTS

VARIA

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Justyna HACHOŁ[1] and Elżbieta BONDAR-NOWAKOWSKA

TENDENCIES IN THE DEVELOPMENT OF HYDROMACROPHYTES AFTER THE COMPLETION OF REGULATORY AND MAINTENANCE WORKS IN A RIVER BED

TENDENCJE W ROZWOJU NACZYNIOWYCH ROŚLIN WODNYCH PO WYKONANIU ROBÓT REGULACYJNYCH I KONSERWACYJNYCH W KORYCIE CIEKU

Abstract: The subject of the following study is the analysis of qualitative and quantitative changes in water plants communities after the completion of regulatory and maintenance works in four Lower Silesian rivers. The field research was conducted in vegetative seasons of 2007, 2008 and 2011 in unmodified, maintained and regulated watercourses. It comprised of an identification of a presence of hydromacrophytes species and the level of the bottom coverage by them. Basing on the results of the research agglomerative analysis allowing identification of the study sections was done. Particular sections were similar in the variability of plants communities. An assessment of species variability and similarities between unmodified and modified communities in a result of works was also performed.

Qualitative and quantitative composition of hydromacrophytes communities after completion of maintenance and regulatory works was changing in time. Species similarity to unmodified sections was higher in the first year after the works completion. However, in the later years the direction of these changes depended on the range of performed works. The structure of hydromacrophytes communities on maintained and regulated sections was getting a lot more similar to the communities structure on the sections excluded from the interference.

Keywords: species similarity, watercourses regulation, maintenance works, water plants

Introduction

Water plants are one of biological components supporting an assessment of ecological state of water [1]. They provide organic substance to the water ecosystem creating environmental conditions in the watercourse and they influence hydro-

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chemistry. They constitute habitats for other water organisms providing food to invertebrates, vertebrates and water related organisms. Water plants have beneficial impact on the watercourses ability to self-purification and decrease of water erosion intensity by the bottom and banks substrate stabilization [2–5].

Simultaneously, strongly developed plants in the watercourse cause elevation of the water level in the river bed and they result in decreasing hydraulic throughput of the river bed [6].

In Poland there was no strategy of plants management in waters in relation to their influence on the river bed throughput and ecological state of the watercourse. Most frequently they are removed from the bottom and banks in a result of regulatory and maintenance works. These plants grow extremely fast resulting in later needs for technical interference in the river bed. Therefore, it is necessary to find the compromise between the range of regulation and maintenance of watercourses and technical requirements and environmental protection.

Regulation of rivers and streams most frequently comprises of the change of technical parameters of the river bed and creation of technical buildings constraining damage resulting from waters and enlarging watercourses usability for common usage of water in national economy [7]. Watercourses maintenance influences the river bed less than regulatory works. It includes all the works resulting in correct outflow of water such as: desludging, water plants and scarps mowing, removal of any impediments hampering the outflow [8–11].

Most authors agree that every technical interference in the river bed influences hydromacrophytes communities directly or indirectly. Direct changes result from technical and technological solutions of conducted works extorting complete removal of plants from the watercourse bottom and scarps [8, 12]. Indirect influence is the result of the following activities: standardisation of cross-section dimensions, removal of stone bars and islands, leveling the bottom and banks. Such activities cause decay of the morphological variety in the river bed and loss of the habitat variety in a consequence species impoverishment of hydromacrophytes communities. Water buildings exert direct influence on water plants. They influence water velocity, changes in the water levels and the kind of the bottom material [13]. Creation of diverse ecosystems above and below the tower point is the result of these [14, 15].

Usually the time of regulatory and maintenance does not exceed several months. Also disruptions of environmental relations caused by the river bed modification have temporal character. Ecosystem regeneration follows them [16–18]. Ecosystem regeneration results in the reconstruction of the organisms community. However, in case of hydromacrophytes creation of the community exactly the same as existing before the disruption is very seldom [12].

This process is not well recognized yet. The results presented in the following study show observations of hydromacrophytes communities reconstruction after the completion of regulatory and maintenance works in four small and medium lowland watercourses. The aim of the research is an assessment of the pace and alternations of quality and quantity directions in these communities.

Methods

Field work was conducted in vegetation seasons of the year 2007, 2008 and 2011 on four Lower Silesian watercourses such as: Dobra, Sasiecznica, Zalina and Zurawka (Table 1).

Table 1

Study objects

Watercourse name	River-mouth	Length of the watercourse [km]
Dobra	Widawa	36.1
Sasiecznica	Barycz	43.9
Zalina	Zurawka	10.9
Zurawka	Sleza	27.5

These watercourses were divided into 13 study sections one hundred meters. They were localized in places of approximate climatic, geologic and soil conditions. Adjacent terrain was agriculturally used with the majority of arable lands. In five study sections there was no dimness while in others it was low or medium. Water in study sections was not contaminated with any municipal or industrial wastes.

The range of works in watercourses was diverse. Therefore study sections should be classified into three groups. The first group comprises of three regulated sections located in Dobra and Zurawka bed. The second group includes watercourses where maintenance works were performed. In case of the section located in the bed of Sasiecznica, interference was very mild as it comprised of manual mowing of the banks and water plants. Other sections located in the bed of Sasiecznica, Zalina and Zurawka maintenance works included manual banks mowing, mechanic desludging and scarps strengthening with fascine. The third group consisted of four study sections, one per each watercourse, set in places where no works were done. They constitute the basis for comparatory analyses. The Table 2 shows detailed characteristic of all study sections.

Field work included identification of hydromacrophytes in the study sections and definition of the their degree of the bottom coverage. All hydromacrophytes both embedded in water for at least 90 % of the vegetative period and higher plants, floating freely on the surface or beneath it were taken into account. Braun-Blanquet five degree scale was used to determine the level of plants density in the river bed [19]. Field work in Dobra, Zalina and Zurawka was performed in 2008 and 2011 while in the Sasiecznica in 2007 and 2011. In all cases the first term of the research was the first vegetation season after the completion of technological works in the river bed.

Results of the field work were analized referring to the assessment of:

– qualitative and quantitative alternations in hydromacrophytes community on modified study sections were a result of technical interference in relation to communities in unmodified beds;

– the influence of the time since the works completion on the qualitative and quantitative composition of hydromacrophytes communities in beds with technical interference.

Table 2

Characteristic of the study sections

Study section		Range of works	Bottom width [m]	Water-course depth [m]	Bottom substrate	Use of the littoral area	Degree of shading[a]	The time from the works completion [the number of wedet periods]	
								Year 2007/2008	Year 2011
Dobra	1	Unmodified section	3.0	1.2	sand	meadows	0	—	—
	2	River bed elutriation, bottom and banks mowing, changes in cross-section parameters, modification of scarps incline to 1:2, strengthening the foundation of riverbank with fascine	3.0	1.0	sand	meadows	0	1	4
	3	Watercourse deepening, changes in cross-section parameters, modification of vertical section with horizontal scarps, strengthening banks with gabions	6.8	2.0	sand/stones	farm buildings/ meadows	0	1	4
Sasiecznica	4	Unmodified section	6.5	1.5	sand	meadows	1	—	—
	5	Bottom and banksmowing	10.0	1:5	sand	meadows	0	1	5
	6	River bed elutriation, bottom and banksmowing, strengthening the foundation of riverbank with fascine	6.0	1:5	sand	meadows	0	1	5
Zalina	7	Unmodified section	1.5	2.1	sand	arable land	1	—	—
	8	River bed elutriation, bottom and banks mowing, river banks zones mowing, strengthening the foundation of riverbank with fascine	2.0	2.0	organic	arable land	1	1	4

Table 2 contd.

Study section		Range of works	Bottom width [m]	Water-course depth [m]	Bottom substrate	Use of the littoral area	Degree of shading[a]	The time from the works completion [the number of wedet periods]	
								Year 2007/2008	Year 2011
Zurawka	9	Unmodified section	3.0	2.2	sand	arable land	2	—	—
	10	River bed elutriation, bottom and banks mowing, river banks zones mowing, strengthening the foundation of riverbank with fascine	3.3	1.4	sand	arable land	1	1	4
	11		3.0	2.0	sand	farm buildings	1	1	4
	12	Watercourse deepening, changes in cross-section parameters, modification of vertical section with horizontal scarps, strengthening banks with retaining wall	6.0	2.0	sand	farm buildings	1	1	4

[a] Degree of shading: 0 – lack of shade, 1 – low, 2 – medium, 3 – high, 4 – full shade.

In order to group study sections according to the diversification of hydromacrophytes communities agglomerative analysis was performed. An assessment of species diversity and similarity of both modified and unmodified communities following works completion was done.

Agglomerative analysis was performed using the Ward method in Statistica v.9 programme. Euclidean distance was accepted as a measure of the distance. Analyzed data included the number of hydromacrophytes species and the degree of the bottom coverage with them. This served as the basis for the division of modified study sections into homogenous groups with respect to the diversification of water plants communities.

Shannon-Wiener – H indicator was used to assess species variability taking into consideration both the number of species and steadiness of their share in the coverage [20]. It was calculated basing on the following formula:

$$H = -\sum_{i=1}^{s} (N_i \cdot \ln N_i)$$

where: H – species variability indicator,
s – the number of hydromacrophytes species in the study section,
N_i – indicator calculated from the formula:

$$N_i = \frac{Q_i}{Q}$$

Q_i – cube of the value of the bottom coverage by plants of i species,
Q – cube of the value of the bottom coverage by plants of all the species.

Species similiarity Jaccard (P) and structures similarity indicators (w_p) were used to assess the level of water plants similarity between modified and unmodified study sections. Species similarity Jaccard indicator was calculated basing on the following formula [8]:

$$P = \frac{2 \cdot C \cdot 100}{A + B}$$

where: P – similarity index [%],
A – the number of species in unmodified study section,
B – the number of species in maintained or regulated study section,
C – the number of common species in compared study sections.

Similarity of structures in water plants communities found in modified and unmodified study sections was determined basing on the number of species with a certain degree of bottom coverage. The index was calculated using the following formula:

$$w_p = \sum_{i=1}^{k} \min (w_{1i}, w_{2i})$$

where: w_p – similarity index between communities structures [%],
w_{1i} – percent share of species in particular classes of the bottom coverage in unmodified sections,
w_{2i} – percent share of species in particular classes of the bottom coverage in modified sections.

Results

Cumulatively 15 species of hydromacrophytes were specified. They included: *Alisma plantago-aquatica* L., *Berula erecta* (Huds.) Coville., *Callitriche* sp., *Ceratophyllum demersum* L., *Elodea canadensis* L., *Glyceria Maxima* (Hartm.) Holmb., *Lemna minor* L., *Myosotis palustris* (L.) L. em. Rchb., *Phalaris arundinacea* L., *Phragmites communis* Trin., *Potamogeton crispus* L., *Potamogeton pectinatus* L., *Sagittaria sagittifolia* L., *Sparganium emersum* Rehmann, *Typha angustifolia* L. Their occurrence and the level of the bottom coverage in particular sections was shown in Table 3.

Data presented in the table shows that in the first vegetation season in 2007 and 2008 13 species of hydromacrophytes were determined together – 8 species in unmodified and 9 in regulated and maintained watercourses. In the vegetation season of 2011 the number of determined species increased to 14.

An increase in the number of species was observed in unmodified sections (13 species) as well as in sections which were maintained and regulated (11 species). The research showed there was a loss of one species (*A. plantago-aquatica*) and two new species of pondweed (*P. crispus* and *P. pectinatus*) appeared. They were not catalogued in the first study season.

Considered watercourses both during the first and second study season showed the most frequent occurrence of *L. minor* and *S. emersum*. Both species were found in 80 % of unmodified sections. In the first season after the works completion these species were present in half of sections under technical activity. In 2011 *L. minor* was found in over 60 % while *S. emersum* in all unmodified sections.

Species which were rarely observed during the field study included: *A. plantago-aquatica* and *C. demersum*. These species were observed only in modified sections while *P. arundinacea*, *P. crispus* and *T. angustifolia* occured in sections without any technical interference.

During the research the most – 8 species of hydromacrophytes were found in unmodified section of Dobra in the second study period and in maintained section of Sasiecznica in the first year of the research. The fewest species were observed in Zurawka section where regulatory work was done. Regulatory works have a very strong level of interferences in the river bed. During the first season after the works completion there were not found any hydromacrophytes in this section. Three years later there was only one species – *S. emersum* found in the section.

Table 3

Hydromacrophytes species and a degree of their bottom coverage in study sections

	Study sections	Dobra			Sasiecznica			Zalina		Zurawka				Σ occurrence
	Aquatic plants	1	2	3	4	5	6	7	8	9	10	11	12	
I study season (2007/2008)	*Alisma plantago-aquatica* L.								1					1
	Berula erecta (Huds.) Coville.	1		1		1								3
	Callitriche sp.		1	1		2			3					4
	Ceratophyllum demersum L.					3								1
	Elodea canadensis L.		5	1	1	2	5							5
	Glyceria Maxima (Hartm.) Holmb.							3						1
	Lemna minor L.	1				2		3	2	3	1	1		7
	Myosotis palustris (L.) L. em. Rchb.	1												1
	Phalaris arundinacea L.	4												1
	Phragmites communis Trin.				5	3	3							3
	Potamogeton crispus L.													0
	Potamogeton pectinatus L.													0
	Sagittaria sagittifolia L.	4				2								2
	Sparganium emersum Rehmann	5	1			2		4	3	4		2		7
	Typha angustifolia L.	3												1
Bottom coverage by all the species		5	5	1	5	3	5	5	4	5	1	2	1	
Number of species		7	3	3	2	8	2	3	4	2	1	2	0	

Table 3 contd.

	Study sections / Aquatic plants	Dobra			Sasiecznica			Zalina		Zurawka				Σ occurrence
		1	2	3	4	5	6	7	8	9	10	11	12	
II study season (2011)	*Alisma plantago-aquatica* L.													0
	Berula erecta (Huds.) Coville.	1	1	1		1	1		1					6
	Callitriche sp.		1			2			4	2		1		5
	Ceratophyllum demersum L.					2								1
	Elodea canadensis L.	1	4	3	1									4
	Glyceria Maxima (Hartm.) Holmb.						1	2			2			3
	Lemna minor L.	1				1	1	2	2	1	2	2		8
	Myosotis palustris (L.) L. em. Rchb.	1					1		1	2				4
	Phalaris arundinacea L.	3												1
	Phragmites communis Trin.				5	4	2							3
	Potamogeton crispus L.									2				1
	Potamogeton pectinatus L.			1						1		1		3
	Sagittaria sagittifolia L.	2	1	1		3			2	1		1		7
	Sparganium emersum Rehmann	4	1	1		1	2	4	3	3	2	3	1	11
	Typha angustifolia L.	2												1
Bottom coverage by all the species		5	4	4	5	5	4	5	4	4	3	3	1	
Number of species		8	5	5	2	7	6	3	6	7	3	5	1	

Conducted research shows that in most cases the number of species after the works completion was higher than in unmodified sections.

Table 3 indicates unmodified sections of watercourses had the highest degree of hydromacrophytes bottom coverage in Braun-Blanquet scale. However, in maintained and regulated watercourses the degree was observed to range between 1 and 5 regardless of the time that has passed from the works completion in the river bed.

Presented data constitute the basis to analysis aiming at regeneration process of hydromacrophytes communities after the completion of regulatory and maintenance works in the bed.

Agglomerative analysis performed to divide study sections into groups of qualitatively and quantitatively homogeneous communities of aquatic plants was done separately for each study period. Watercourses where works were performed were the only to be taken into account. They resulted in a complete elimination of aquatic plants in every section therefore, in starting point they were identical. Agglomerative analysis served as a basis to obtain two dendrograms presented in the Fig. 1a and 1b.

Figure 1a shows that study sections in the first vegetation period after the completion of maintenance and regulatory works create three agglomerates (23 Euclidean distance).

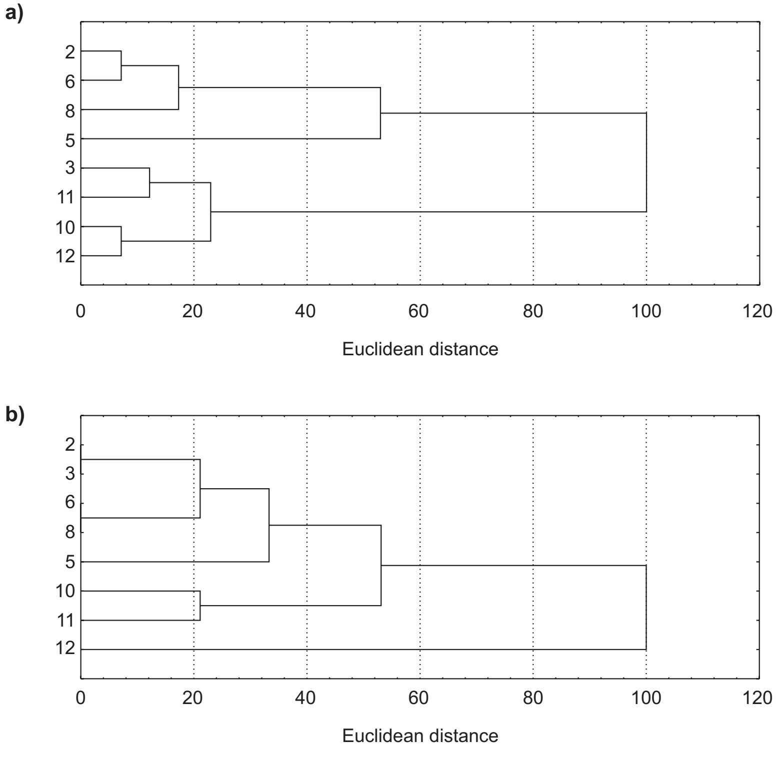

Fig. 1. Classification of modified study sections into homogeneous groups with respect to their qualitative and qantitative composition in hydromacrophytes communities basing on agglomerative analysis: a) – in the I, b) – in the II study period

The first agglomerate comprises two sections where regulatory works were performed (6, 8) and one regulated section (2). Common characteristic of these three sections are scarps strengthened with fascine. Section no. 5 where maintenance works were limited to mowing of scarps and plants in the bottom of the river bed differs distinctly from other study sections and it constitutes separate agglomerates. The third concentration includes both regulated (3, 12) and maintained (10, 11) sections.

Figure 1b suggests that in the later study period variety of the composition of hydromacrophytes has grown and it is possible to distinguish four agglomerates (33 Euclidean distance). The first comprises of two sections located in maintenance watercourses (6, 8) and two other are located in regulated watercourses (2, 3). Section no. 5 similarly as in the first study period constitutes separate agglomerates. Subsequent agglomerate contains two sections located in maintained river bed of Zurawka. Section no. 12 also found in this watercourse but regulated, showed a considerable difference from the other study sections. Euclidean distance of 100 (Fig. 1b) indicates this.

Performed analysis shows that in the first vegetative season after the works completion, qualitative and quantitative composition of aquatic plants communities in the study sections was not linked with the range of conducted works. Regulated and maintained sections such as 2 and 6, 3 and 11, 10 and 12 revealed similar composition of plant communities. The only distinguishing section was section no. 5 with limited range of works. In the later study season a certain tendency might be observed. An increase in the similarity of aquatic plants communities composition in study sections with similar works range was reported (2 and 3; 6 and 8; 10 and 11; 5; 12). In order to understand the following tendency better subsequent analyses were performed separately for each section.

Index of species diversity was calculated for all sections in both study periods. Its values and change tendencies in the study season were shown in the Fig. 2. Vertical axes show Shannon-Wiener values in two study periods while arrows represent particular sections of watercourses. They indicate corresponding values of the indicator itself and its change tendencies.

The analysis of the figure reveals that the indicator of diversity was accepted between 0–1.92. In the two following watercourses: Dobra (sections 1–3) and Zurawka (sections between 9 and 12) higher indicators of diversity occurred in unmodified sections. In compared sections of Zalina river *H* values were approximate. In unmodified Sasiecznica section values of species diversity were lower than in compared unmodified sections.

The highest species diversity was noted in the section no. 5 located in Sasiecznica river in the first vegetative season after the works completion. Four years later significant domination of two species was noted. It resulted in a reduction of Shannon-Wiener indicator. In other sections located in modified river beds values of the diversity indicator during second study period were similar or higher than directly after the works completion.

The lowest values of Shannon-Wiener Index were noted in sections 3 and 12 where vertical, tightly consolidated banks were performed.

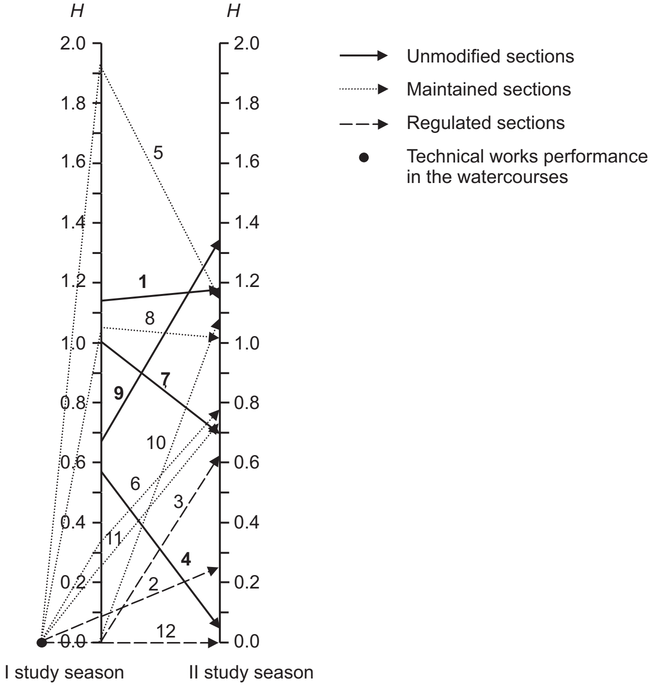

Fig. 2. A tendency in changes of the species diversity indicator in study sections

Presented data suggest that regulatory in comparison with maintenance work had greater impact on changes in species diversity expressed by Shannon-Wiener indicator.

Similarity between communities of hydromacrophytes occurring in sections where regulatory and maintenance works were performed and equivalent of unmodified watercourses were determined basing on species and communities structure (w_p) and indicators of similarity (P). Calculations were done for both study periods. Results of this analysis are presented in Fig. 3a and b.

Fig. 3a shows the diversity in the impact of regulatory and maintenance works on hydromacrophytes communities. While the works were realized regardless of their range, aquatic plants were removed from the bottom of the watercourse completely. Species similarity to unmodified sections was the same in all cases and it amounted to 0 %.

During the first vegetative season after the completion of works some species appeared in watercourses again causing species similarity of compared sections to grow in case of all maintained (5, 6, 8, 10, 11) and two regulated sections (2, 3). The following tendency was sustained during later years only in case of sections where regulatory works were conducted. In all maintained sections species similarity to compared sections revealed significant downward tendency. Perhaps after better identification this characteristic may be used for an assessment of the modification degree of the river bed.

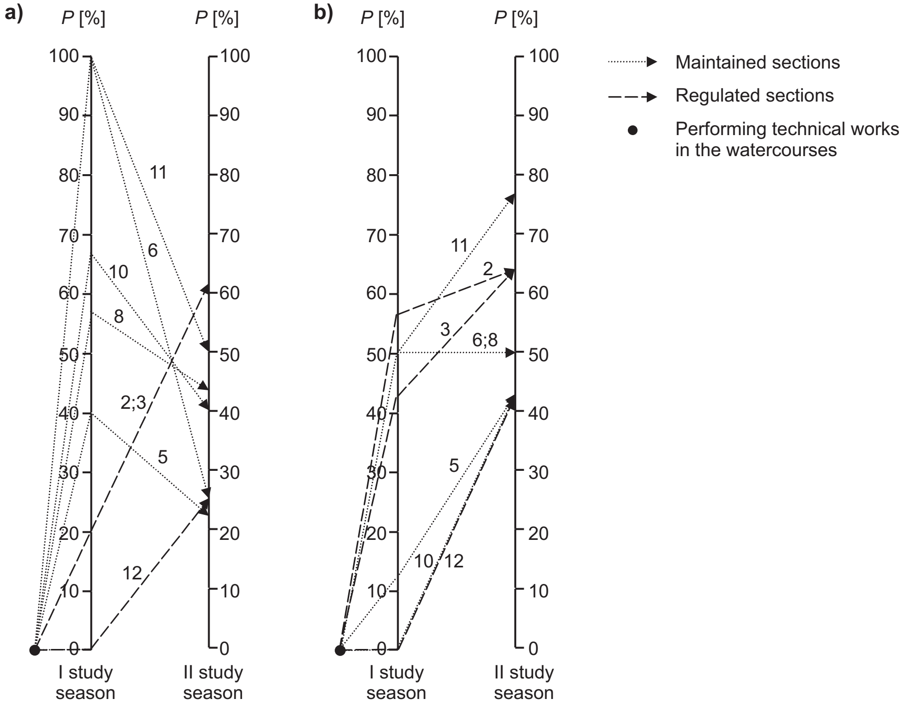

Fig. 3. Species (a) and communities structures of hydromacrophytes (b) similarity in two study periods

Different relation was observed in case of similarity among communities structures. Fig. 3b shows that structure of aquatic plants communities considering the number of species and their share in the coverage in all modified sections was becoming more approximate to the structure of communities in sections not being a subject of such intrusion.

Discussion

In the study sections 15 species of hydromacrophytes were determined altogether. They are ordinarily and commonly found taxons in waters of Polish lowland. The number of species occurring in modified sections as a result of works and unmodified sections was similar. These values are low in comparison with values found by authors conducting similar research [9, 21–23]. Low number of aquatic plants determined during the field work may be caused by the fact that analyzed watercourses were located in scarcely varied agricultural landscape and they were under technical intrusion before.

Agglomerative analysis showed that in the first vegetative season after the works completion qualitative and quantitative composition of aquatic plants communities was not related to their range. It results from the fact that both in maintenance and regulatory works aquatic plants were removed from the river bed entirely [8, 12] and they developed similarly in the initial period after works completion regardless of the sort of technical activities. An increase in composition similarity of examined communities of sections with the same works range was noted. This may show that the range of works impacted aquatic plants composition after a certain time from their completion.

The highest species diversity was noted in the section maintained during the first vegetative season after the works completion. Removal of plants covering banks, shading river bed and also expansive reed plants resulted in an improvement of habitat conditions for aquatic plants. They could develop steadily which influenced high indicator of biodiversity. It may be a confirmation of many authors' view that correctly conducted maintenance works taking into account ecological requirements may have beneficial impact on environmental system of the watercourse [8, 24, 25].

The lowest species diversity was reported in sections 3 and 12 where vertical, tightly strengthened banks were made. They constituted a barrier for substances influx to the watercourse from its drainage area [26, 27]. Moreover change in cross-section parameters impacted changes in hydraulic characteristics of both rivers. In a consequence it is inevitable to disturb existing dynamic balance of the river and its environment resulting in its ecological threat [25].

Conducted analysis of similarity between species and structures shows the process of the watercourse overgrowing begins very fast after the works completion. In the first vegetative season after their accomplishment an average indicator of similarity in the sections located in both modified and unmodified watercourses was amounted to 50 %. However, an average similarity of hydromacrophytes communities in compared sections was lower and it was measured at 33 %. Similar tendencies were observed by Fox and Murphy [12]. While examining an influence of aquatic plants removal in 4 British watercourses they claimed that each interference of the same kind results in the reduction of plants species biodiversity. In later years species similarity in relation to comparative sections revealed clear decreasing tendency in all sections of maintained watercourses while in regulated sections similarity grew higher. These tendencies as well as the results of performed agglomerative analysis may show that the range of works influences a composition of aquatic plants species after a certain time after their completion. However, plants communities structure of all modified sections was getting approximate to the structure in unmodified sections.

Performed research shows that qualitative and quantitative changes in aquatic plants communities resulting from regulatory and maintenance works in the river bed should be assessed concerning the time indicator. Regardless of the range of works disrupting environmental relations caused by modifications in the watercourse they all led to ecosystem regeneration. The result indicates secondary succession in watercourses not being a subject to assessment. This process was a subject of study for Hearne and Armitage [28], Krebs [17], Lampert and Sommer [18], Falinska [16]. Secondary succession is connected with the fact that most aquatic plants have extremely effective mechanisms of vegetative reproduction and expansion [29, 30]. In a result of secondary succession it is possible for the group of particular organisms to restore plants community inhabiting the watercourse before the works conduction. However, hardy ever do we observe creation of an ecosystem identical to the previous one [12]. It was confirmed by conducted research.

Conclusions

The following conclusions were drawn from performed research:

1. Field work conducted in four lowland watercourses showed that regulatory and maintenance works had an impact on the qualitative and quantitative composition of hydromacrophytes communities.
2. This composition was changing in time both in modified and unmodified sections.
3. In the first vegetative season after the completion of works in the river bed tendencies in recreation of plant communities were not connected with their range. This relation was observed in the next research period.
4. In modified sections as a result of technical interference, species similarity to unmodified sections was increasing in the first year after the works completion. In maintained sections after 4–5 years from the works completion, species similarity between compared sections was lower than in the first year while in regulated sections a high increase in species similarity was observed.
5. In the course of time from technical interference in the river bed the structure of plant communities in all modified sections was getting closer to the structure of aquatic plants communities in sections not being a subject of interference.

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TENDENCJE W ROZWOJU NACZYNIOWYCH ROŚLIN WODNYCH PO WYKONANIU ROBÓT REGULACYJNYCH I KONSERWACYJNYCH W KORYCIE CIEKU

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Abstrakt: Przedmiotem pracy jest analiza zmian jakościowych i ilościowych w zbiorowiskach naczyniowych roślin wodnych po wykonaniu robót regulacyjnych i konserwacyjnych w czterech ciekach nizinnych Dolnego Śląska. Badania terenowe prowadzono w sezonach wegetacyjnych 2007, 2008 i 2011 r. na ciekach nieprzekształconych, konserwowanych oraz regulowanych. Obejmowały one identyfikację występujących w korycie gatunków naczyniowych roślin wodnych oraz określenie stopnia pokrycia przez nie dna. Na podstawie wyników badań wykonano analizę skupień, pozwalającą na pogrupowanie odcinków badawczych, podobnych pod względem zróżnicowania zbiorowisk roślin wodnych. Dokonano również oceny różnorodności gatunkowej oraz oceniono podobieństwo zbiorowisk nieprzekształconych i przekształconych w następstwie robót.

Skład jakościowy i ilościowy zbiorowisk naczyniowych roślin wodnych po wykonaniu w korycie robót konserwacyjnych i regulacyjnych zmieniał się w czasie. Podobieństwo gatunkowe do odcinków nieprzekształconych wzrastało w pierwszym roku po zakończeniu robót. Natomiast w kolejnych latach kierunek tych zmian zależał od zakresu przeprowadzonych prac. Struktura zbiorowisk roślinnych na odcinkach konserwowanych i regulowanych z czasem stawała się coraz bardziej zbliżona do struktury zbiorowisk na odcinkach nieobjętych tą ingerencją.

Słowa kluczowe: podobieństwo gatunkowe, regulacja cieków, roboty konserwacyjne, rośliny wodne

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EFFECT OF SEWAGE SLUDGE ON BIOMASS PRODUCTION AND CONTENT OF MACRONUTRIENTS AND CHLOROPHYLL IN GRASS MIXTURES

WPŁYW OSADU ŚCIEKOWEGO NA PRODUKCJĘ BIOMASY I ZAWARTOŚĆ MAKROSKŁADNIKÓW ORAZ CHLOROFILU W MIESZANKACH TRAW

Abstract: The aim of this study was to determine the effect of various doses of municipal sewage sludge on the growth of biomass of aboveground parts of lawn grass mixtures and their macronutrients and chlorophyll content. Four experiments on the lawns along the main roads of Bialystok (at Popieluszki, Hetmanska, Piastowska and Raginisa Strs.) were founded. Three doses of sewage sludge (0.0 – control; 7.5 and 15.0 kg $\cdot$ m^{-2}) and two grass mixtures: Eko and Roadside were factors in experiment. Samples of aboveground part of grasses were collected 3 times: in June, August and October 2011, after that dry matter of the aboveground part of grasses from 1 m^2, the total nitrogen content, total phosphorus content, total potassium content and chlorophyll *a* and *b* content were determined. The dose of sewage sludge significantly influenced N and K accumulation in the grasses. The maximum average nitrogen content (2.82 % of d.m.) was observed in grass from plots with the highest dose of sewage sludge, while the potassium from plots with sewage sludge dose 7.5 kg $\cdot$ m^{-2}. The accumulation of biomass of grasses in the study period was mainly differentiated by the sewage sludge dose and the sampling time. The average summary yield for the three months study (June, August and October) was from 229.83 to 430.70 g $\cdot$ m^{-2}. The highest results were obtained at a dose of sewage sludge 15.0 kg $\cdot$ m^{-2}. The sampling time and dose of sewage sludge significantly influenced chlorophyll *a* and *b* content. The average chlorophyll *a* content in June, August and October was: 0.60; 0.64 and 0.54 mg $\cdot$ g^{-1} of f.m. respectively, while chlorophyll *b*: 1.00; 0.94; 0.39 mg $\cdot$ g^{-1} of f.m. It was found a low average ratio of chlorophyll *a* to *b* in mixtures of grasses, which ranged from 0.54 in June to 1.82 in October to mixture Eco and 0.57 in June to 1.68 in October to mixture Roadside. Plants of the control plots showed higher average ratio of chlorophyll *a* to *b* in comparison with plants from plots with sewage sludge amendment.

Keywords: biomass, lawn grasses, macronutrients, chlorophyll, sewage sludge

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Introduction

Disposal of sewage sludge is becoming an increasing problem due to the increasing amount of biosolids. The main reason of this situation is the fact that amount of treated wastewater is increasing, which is associated with the dynamic development of sewerage system. Measurable result is an increasing percentage of the population supported by sewage treatment and a continuous increase in amount of municipal sewage sludge [1]. Therefore, it is necessary search for methods and ways of rational use of this biosolid.

One way of utilization of municipal sewage sludge is to use it for recultivation of degraded areas, biological fixation of surface from wind or water erosion or to improve water retention and possible fertilization of plants not intended for human consumption [2, 3]. It is justified by the fertilizer properties of the sewage sludge such as high content of nitrogen, phosphorus, carbon, macro- and microelements, which are necessary to improve soil conditions and plant growth [4–7]. Moreover, due to the high content of organic matter in biosolid, it is possible to improve soil physical properties such as soil aeration and its water holding capacity, helping to improve soil microbial activity, *eg* respiration and enzymatic activity [7–9]. Therefore, very promising future area of application of municipal sewage sludge is land adjacent to roads. Urban soils are usually formed from building waste, which means that their structure is more dense, have lower content of humus, lower water capacity and water permeability, and lower biological activity [10]. Furthermore, developing industry and transport communications are threats for urban soils because of their progressive chemical degradation that leads to a sustainable and progressive deterioration of their properties. It is a reason that urban soils require recultivation treatment [11].

Green city areas, including lawns, have various kinds of functions. On the one hand, well cared lawns enhance the aesthetic value of the city, on the other hand, play phytoremediation role, both for the air and soil generated by transport [12].

For the effective phytoremediation plants should be characterized by high resistance to difficult environmental conditions, have the ability to accumulate xenobiotics from the soil, as well as rapid growth and high dry mass production. Grasses are characterized by high phytoremediation potential [13]. Grasses in urban areas can fulfill the above requirements when they have good conditions for rapid growth and high dry mass production.

The aim of this paper was to assess the effect of different doses of municipal sewage sludge for the production of dry mass of lawn grass mixtures and the contents of nitrogen, phosphorus, potassium, chlorophyll *a* and *b* and the ratio of chlorophyll *a* to *b* in urban lawn grasses.

Materials and methods

Four experiments on the lawns along the main roads of Bialystok: Popiełuszki Str., Hetmańska Str., Piastowska Str. and Raginisa Str. were founded. Each experimental area was 90 m^2 and each of them was divided into 18 plots with 5 m^2 area. The factors of the experiment were: 3 doses of sewage sludge and two mixtures of lawn grasses.

Municipal sewage sludge from the Municipal Wastewater Treatment Plant in Sokolka was used. Sewage sludge was stabilized and had a smear texture. For fertilization 3 doses of sewage sludge: 0.0, 7.5 and 15.0 kg · m^{-2} were used. Doses of sewage sludge were established according to Kiryluk [14] who found in several years study that the most effective doses for turfing of municipal waste disposal areas were those above 40 Mg/ha. Sewage sludge in autumn 2010 was used.

Before establishment of experiment both sewage sludge and soil from each combination were analyzed according to Directive of Evironmental Minister from July 13th, 2010 concerning municipal sewage sludges [2]. Analyzes were done by Regional Chemical and Agricultural Station in Bialystok (Tables 1 and 2).

Table 1

Selected physical and chemical properties of soils

Properties	Popieluszki	Hetmanska	Piastowska	Raginisa
pH	7.6	7.9	7.7	7.4
Sand [%]	75.69	75.89	71.87	84.35
Silt [%]	22.30	22.02	25.41	14.67
Clay [%]	2.01	2.09	2.72	0.98
Textural class	loamy sand	loamy sand	sandy loam	sand
P_2O_5 [mg/100 g]	22.0	7.3	18.4	10.0

Table 2

Selected properties of municipal sewage sludge

Properties	Municipal sewage sludge
pH	6.7
Dry weight [%]	19.30
Organic matter [% d.m.]	58.40
Total P [% d.m.]	2.73
Total N [% d.m.]	3.99
Ammonium N [% d.m.]	0.14
Ca [% d.m.]	5.51
Mg [% d.m.]	0.66
Pb [mg/kg d.m.]	23.5
Cd [mg/kg d.m.]	< 0.50
Cr [mg/kg d.m.]	58.00
Cu [mg/kg d.m.]	194.00
Ni [mg/kg d.m.]	22.00
Zn [mg/kg d.m.]	1459.00
Hg [mg/kg d.m.]	1.04

In spring 2011, on the prepared plots two mixtures of lawn grasses were seeded: Eko (M1) from Nieznanice Plant Breeding Station which included 30 % of *Lolium perenne* cv. Niga, 15 % of *Poa pratensis* cv. Amason, 22.6 % of *Festuca rubra* cv. Adio and 32.4 % of *Festuca rubra* cv. Nimba. and grass mixture Roadside (M2) from Barenbrug which included 32 % of *Lolium perenne* cv. Barmedia, 5 % of *Poa pratensis* cv. Baron, 52 % of *Festuca rubra rubra* cv. Barustic, 5 % of *Festuca rubra commutata* cv. Bardiva (BE) and 6 % of *Festuca rubra commutata* cv. Bardiva (NL).

There were obtained 72 test plots (4 locations 2 grass mixtures 3 doses of sewage sludge 3 replicates), each with 5 m^2 area.

Dry matter of the aboveground part of grasses from 1 m^2, total nitrogen content, total phosphorus content, total potassium content and chlorophyll *a* and *b* content were determined in grass samples collected in June (27.06.2011), August (16.08.2011) and October (14.10.2011). Aboveground parts of grass mixture were also harvested 21.07.2011 and 18.09.2011 and their dry matter was detrminated, but macronutrient and chlorophyll contents were not determined.

Aboveground parts of plants were cut from a random 33.3 × 33.3 cm area of each plot in order to determine dry matter. Grass samples were dried at 105 ^oC for 24 h, then at 75 ^oC, for complete water evaporation.

Total nitrogen in aboveground parts of grass was determined by the Kjeldahl method after sample mineralization in concentrated sulfuric acid [15].

Total phosphorus in aboveground parts of grasses was determined by molibdo-vanadate method after sample mineralization in concentrated sulfuric acid with hydrogen peroxide [15].

Total potassium concentration in plant material were determined using *Atomic Absorption Spectrometry* AAS (Varian SpectrAA-100A). Samples were mineralized in temperature about 450 ^oC and ashes were dissolved in concentrated nitric(V) acid.

For chlorophyll determination fresh plant material was homogenized in a mortar with addition of $CaCO_3$ and quartz sand. Chlorophyll was extracted with 80 % acetone. Chlorophyll *a* and *b* content was determined using HACH DR5000 spectrophotometer by measuring absorbance at $\lambda = 663$ and 645 nm. The content of chlorophyll *a* and *b* were calculated according to the formulas:

$$\text{Chlorophyll } a = (12.7 \cdot D_{663} - 2.7 \cdot D_{645}) \cdot V \cdot (1000\ w)^{-1}$$

$$\text{Chlorophyll } b = (22.9 \cdot D_{645} - 4.7 \cdot D_{663}) \cdot V \cdot (1000\ w)^{-1}$$

where: D_{645} and D_{663} – optical density at $\lambda = 645$ and 663 nm, respectively,
V – volume of the solution in [cm^3],
w – fresh weight of the leaves sample in [g].

The results were statistically analyzed using analysis of variance with Tukey test at significance level at $\alpha = 0.05$. The correlation between characteristics were calculated using Statistica 9.0.

Results and discussion

One of the consequences of the use of sewage sludge for plant fertilization may be change of plant chemical composition. The nutrients contained in biosolid are beneficial for plant growth and development. On the other hand, the introduction of the sludge to the soil also entails risk of the circulation of heavy metals and other contaminants, which can cause adverse effects on physiological processes in plants [16]. Municipal sewage sludge used in the experiment satisfied the requirements of Regulation [3] on the application of sewage sludge to non-agricultural land recultivation. Furthermore, sludge are characterized by a high abundance of nitrogen and phosphorus, and the organic matter (Table 2). Municipal sewage sludge fertilization influenced concentration of nitrogen, potassium, chlorophyll *a* and *b* in plants and the accumulation of aboveground dry matter of grasses.

Uptake and use of minerals by plants from sludge is dependent on many factors *ie* holding water capacity, redox potential, soil temperature, microbial activity in the rhizosphere. Each of this factors (either alone or in combination with the others) can stimulate or inhibit mineral uptake by the plant and its impact on their chemical composition [17].

Nitrogen is an element that plants take in the largest quantities. This is mainly due to the fact that it is a part not only of amino acids and proteins but also the nucleotides (such as adenosine-5'-triphosphate – ATP) and nucleic acids, some of the plant hormones, some of secondary metabolites, and other biologically important compounds [18]. Several studies have shown that nitrogen is one of the most important elements of yielding, and nitrogen fertilization is especially effective when the soil is rich in other nutrients [19].

The nitrogen concentration in the used grass mixtures was differentiated, but statistically insignificant. Factors that influenced the nitrogen concentration of the studied grasses were biosolid dose, sampling time and location (Table 3).

The lowest average concentrations of total nitrogen were observed in control plants (1.90 % of d.m.). Addition of the sludge to the soil resulted in increase of nitrogen concentration in grasses (on average 38.0 %) compared with control plots. Similar results were obtained by Gondek and Filipek-Mazur [20], who found higher nitrogen concentration in white mustard after the application of sewage sludge than without fertilization. The highest nitrogen concentration in the plant samples (2.80 %) collected from the plots with the highest dose sludge was observed. Sewage sludge used in the study of Jama and Nowak [21] caused increase of nitrogen concentration in the leaves of willow at a single dose (75.0 Mg (t)/ha), while double dose caused a decline of this component.

The average concentration of nitrogen in grass mixtures was lowest in samples collected in October (2.06 % of d.m.) and the highest in samples of August (2.54 % of d.m.). Nitrogen in the sludge mainly occurs in organic form [22]. Sewage sludge amendment causes intensive soil microbial activity and intensive development of rhizosphere [23, 24]. As a result of progressive mineralization of organic nitrogen, its mineral forms (NO_3^- and NH_4^+) are released and nitrogen becomes available to plants in optimum amounts [9, 25]. Availability of nutrients from sewage sludge is a function of climatic conditions during vegetation period, dose of sewage sludge and sludge C to N ratio [19]. Decrease in temperature reduces activity of soil microorganisms which are responsible for decomposition of organic matter [24]. October is the month when plant vegetation is ceasing and plant demand for this component decreases. Furthermore, the biochemical processes occurring in the soil are inhibited and intensity of release of nitrogen is lower.

Table 3

Total nitrogen, phosphorus and potassium concentration [% of d.m.] in aboveground parts of grass mixtures (ECO and ROADSIDE) grown in Bialystok at Popieluszki, Hetmanska, Piastowska and Raginisa streets. Plants were harvested in June, August and October 2011

Factor	N [% of d.m.]	P [% of d.m.]	K [% of d.m.]	Dry matter [g · m^{-2}]
A – grass mixtures				
Eko	2.33	0.25	1.60	111.14
Roadside	2.42	0.24	1.49	113.76
LSD$_{0.05}$	ns.*	ns.	0.80	ns.
B – dose of sewage sludge				
0.0 kg · m^{-2}	1.90	0.24	1.45	76.61
7.5 kg · m^{-2}	2.41	0.23	1.63	117.17
15.0 kg · m^{-2}	2.82	0.27	1.57	143.57
LSD$_{0.05}$	0.15	ns.	0.11	14.19
C – time of sampling				
June	2.52	0.24	1.73	158.37
August	2.54	0.22	1.78	126.70
October	2.06	0.27	1.13	52.28
LSD$_{0.05}$	0.15	ns.	0.11	14.19
D – localization				
Popieluszki St.	2.26	0.27	1.36	83.22
Hetmanska St.	2.17	0.22	1.46	105.55
Piastowska St.	2.22	0,24	1,82	154.73
Raginisa St.	2.84	0.25	1.55	106.30
LSD$_{0.05}$	0.20	ns.	0.15	18.25

* not significant differences.

Average accumulation of nitrogen by mixtures of lawn grasses was the highest at Raginisa Str. (2.84 % of d.m.), while the lowest at Hetmanska Str. (2.17 % of d.m.). It can be assumed that intensity of accumulation of this component by plants largely depended on soil condition at the given location and the velocity of mineralization of organic matter (C : N ratio in the soil mainly) as Gondek [19] was reported.

Phosphorus, like nitrogen, is an essential macronutrient for plant growth. Phosphorus concentration in the grasses in each time of the study was similar independently of all studied factors (Table 3). This indicates that the sewage sludge amendment did not influence the amount of this component in the aboveground parts of grass mixtures. Similar results obtained Jakubus [15]. The author argues that phosphorus from sewage sludge as compared with other biogenic elements was the least used by plants. This is probably due to occurrence of this element in the forms of sparingly soluble and, therefore sparingly available to plants. Phosphorus in the soil undergoes strong chemical sorption. The rate of release of this component depends largely on the soil pH [20]. It should be noted that soil amendment with sewage sludge showed high pH in the range 7.4–7.9 (Table 1), which is characteristic for urban soils, which are usually created with debris-limestone additives and high pH they may be also caused by precipitation of alkaline dust [26]. Alkaline soil pH (above 7) may cause immobilization of phosphorus by forming its compounds with calcium and that entails, limiting its availability. Furthermore, no difference in phosphorus concentration in plants after application of sewage sludge may be due to low susceptibility to degradation of sewage sludge [27]. Various sludge mineralization rate determines the various degrees of nutrients release, and thus, their availability for plants.

Another component which grasses collect in large quantities is potassium. In our research all the experimental factors had a significant impact on the content of potassium in the aboveground part of grasses (Table 3). In average 7.40 % more potassium accumulated grass mixture Eko than Roadside. Taking into account dose of sludge, in average the most potassium accumulated grasses from plots, where 7.5 kg/m^2 of sewage sludge was used (1.63 % of d.m.) (Table 3). Grass fertilized with 15 kg/m^2 of sewage sludge and without fertilization accumulated 4.00 % and 12.40 % less potassium compared with plots with a single sewage sludge dose. The results are not reflected in the research of Harnisz and Ciecko [28], where they did not observed effect of sludge fertilizer on the potassium concentration in green mass of corn. A higher potassium concentration in the grasses collected in August and June was founded, but less in October (1.78, 1.73 and 1.13 % d.m., respectively). On average the highest accumulation of potassium in the dry mass was in grass from Piastowska Str. (1.82 % d.m.) and the lowest from Popieluszki Str. (1.36 % of d.m.). According to the literature, potassium concentration in dry matter of plants is high and ranges from 2 to 5 %. Our studies indicate a low level of this element concentration in the test grass mixtures. According to many authors [7, 4, 29] potassium concentration in sewage sludge is low, because good solubility of potassium compounds what is a reason for its discharge with wastewater. Siuta [4] and Tujaka [29] paid attention to the fact that the use of sewage sludge to fertilizertion and recultivation should be supplemented with potassium. This is especially important because of the low levels of nutrients in urban soils. Ciecko and Harnisz [28] stated higher potassium content in plants after fertilization with sewage sludge compost with manure and straw, which was an additional source of potassium. Our results indicate that sewage sludge application without addition components rich with potassium does not meet needs of the plants for this component.

Dry matter production is an indicator of soil fertility and plant production potential [30]. The accumulation of dry matter by aboveground lawn grass mixtures in the study period was differentiated by the sewage sludge dose, the sampling time and location (Table 3). The average summary dry matter for the study period (June, August and October) was from 229.83 to 430.70 g $\cdot$ m^{-2}. Summary production of biomass from the plots with sewage sludge increased on average by 70 % compared with the plots without biosolids. The best results were obtained by using a double dose of sewage sludge. Taking into account the sampling time, the maximum average dry matter was in June (158.37 g · m^{-2}). The minimum yield of dry matter was observed in October (52.28 g · m^{-2}). On average the largest dry matter during one harvest was obtained from plots on Piastowska Str. (154.73 g · m^{-2}), while the smallest on Popiełuszki Str. (83.22 g · m^{-2}). The studied dry matter of grass mixtures varied, but not statistically significant (Table 3).

Many authors supports yielding role of sewage sludge [16, 19, 30]. According to Gondek [19], production of dry matter and its chemical composition is highly modified not only as a result of fertilizer application but also as a result organic compounds transformation in soil. This transformation depends on frequently changing environmental factors.

Statistical analysis showed that the concentration of potassium and nitrogen in plant is correlated with the amount of dry matter and the correlation coefficients are r = 0.60 and 0.39, respectively. This confirms the fact that nitrogen and potassium are one of a major elements which determine an increase of dry matter as also provides Kutik et al [31]. According to Starck [32], production of dry matter is manly a result of photosynthetic activity of plants and nitrogen assimilation, which activate growth processes, *eg* in increase of assimilation area of leaves and better plant development [33].

Chlorophyll concentration in leaves is a factor, which can determine plant dry matter, as it allows a plant to trap solar energy and to produce assimilates [34].

Our study shows that municipal soil amendment sewage sludge influenced chlorophyll *a* and *b* concentration in lawn grass mixtures and their ratio. The concentration of chlorophyll *a* in aboveground parts of grasses was dependent on the used grass mixture, harvest time, location and to a lesser extent on the dose of sewage sludge (Table 4). The highest average concentration of chlorophyll *a* was found in August (0.64 mg · g^{-1} of f.m.) and the smallest in samples collected in October (0.54 mg · g^{-1} of f.m.). An average chlorophyll *a* concentration was higher by 5.20 % in Roadside mixture than in Eko mixture (0.58 mg · g^{-1} of f.m.). Average chlorophyll a content was the highest in the grass collected from Piastowska Str. (0.63 mg · g^{-1} of f.m.) and the lowest from Popiełuszki Str. (0.56 mg · g^{-1} of f.m.). A sewage sludge fertilization increased the chlorophyll *a* concentration in average by 3.4 % compared with control plots (Table 4).

The concentration of chlorophyll *b* was differentiated by dose of sludge and sampling time (Table 4). The highest average chlorophyll *b* concentration in the grass samples collected in June was found (1.00 mg · g^{-1} of f.m.) and the lowest in a samples in October (0.39 mg · g^{-1} of f.m.). The increase concentration of chlorophyll *b* was proportional to the dose of sewage sludge. Sewage sludge resulted in its increase of average concentration of 37.10 % compared with control plots (0.62 mg · g^{-1} of f.m.).

Results of our study suggest that one of the differentiating factors of chlorophyll concentration is a kind of grass mixtures. This confirms the observations of Gebczynski [35], who suggests that a level of chlorophyll *a*+*b* in plants may fluctuate and one of the major factor of variation of this parameter can be a strain. Additionally these results show that sewage sludge differentiated chlorophyll concentration. It is not confirmed by Woloszyk and Maciorowski [36] who worked with rape and winter wheat, and used sewage sludge compost. They had no effect on a chlorophyll content in a leaves.

Table 4

Average chlorophyll *a* and *b* concentration [mg/g f.m.] in aboveground parts of grass mixtures (ECO and Roadside) grown in Bialystok at Popieluszki, Hetmanska, Piastowska and Raginisa streets. Plants were harvested in June, August and October 2011

Factor	chl *a* [mg/g f.m.]	chl *b* [mg/g f.m.]
A – grass mixtures		
Eko	0.58	0.77
Roadside	0.61	0.78
$LSD_{0.05}$	0.02	ns.*
B – dose of sewage sludge		
0.0	0.58	0.62
7.5	0.59	0.81
15.0	0.61	0.89
$LSD_{0.05}$	0.03	0.07
C – time of sampling		
June	0.60	1.00
August	0.64	0.94
October	0.54	0.39
$LSD_{0.05}$	0.03	0.07
D – localization		
Popieluszki St.	0.56	0.76
Hetmanska St.	0.58	0.74
Piastowska St.	0.63	0.81
Raginisa St.	0.60	0.79
$LSD_{0.05}$	0.04	ns.

* ns. – not significant differences.

Kachel-Jakubowska [37] highlights that chlorophyll concentration is correlated with nitrogen concentration, which is a component of chlorophyll [33]. The correlation coefficients obtained in our study (r = 0.33 and r = 0.58) confirm relation of chlorophyll *a* and *b* with nitrogen concentration in the grass and positive correlation of chlorophyll *a* and *b* concentration with biomass production (r = 0.41 and r = 0.47). Swedrzynska et al [38] in research on corn and oats found that, when nitrogen fertilization increased, level of chlorophyll and aboveground dry matter increased significantly. According to Ciecko et al [39], potassium is also responsible for increasing concentration of chlorophyll in assimilatory parts, which justifies the resulting correlation between the component of grasses and chlorophyll *a* and *b* concentration (r = 0.34 and 0.67).

The ratio of chlorophyll *a* to chlorophyll *b* was varied in studied grass in all experimental plots. Taking into account the location of grass mixtures, the highest and lowest average chlorophyll *a* to *b* ratios in plants growing on plots from Raginisa Str. was observed and it was from 0.64 to 1.15 for Eco mixture and from 0.63 to 1.02 for

Roadside mixture (Fig. 1a, 1d). Taking into account the sample time collection, the average ratio of chlorophyll *a* to *b* was from 0.54 in June to 1.82 in October for Eko mixture and from 0.57 in June to 1.68 in October for Roadside mixture (Fig. 1a, 1b).

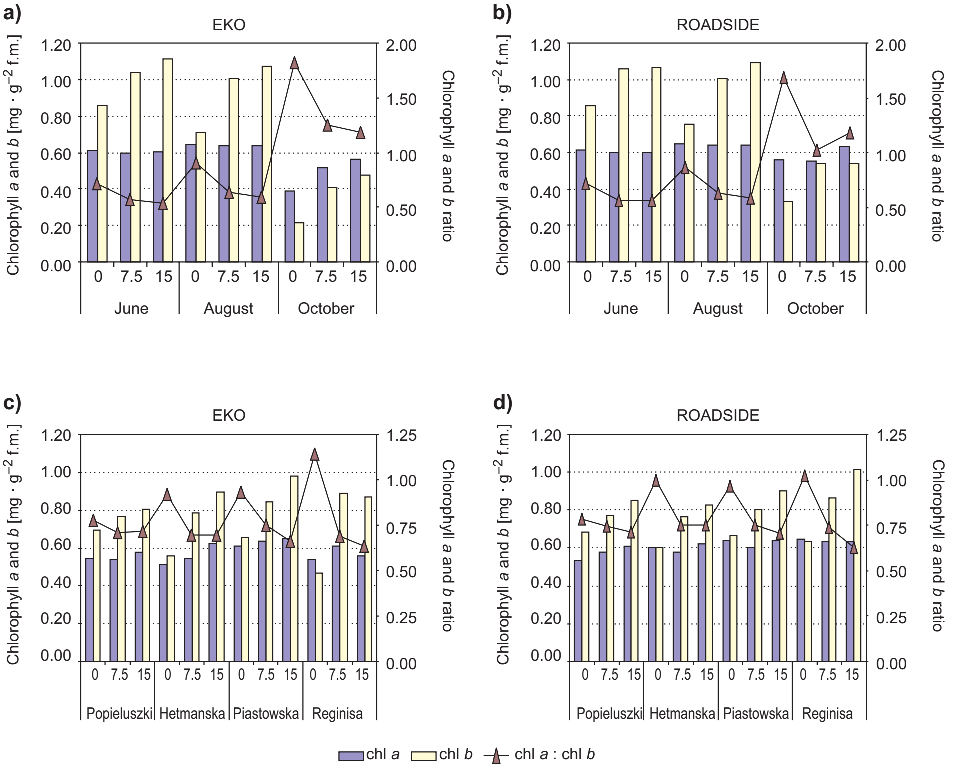

Fig. 1. Average chlorophyl *a* and *b* concentration [mg · g^{-1} of f.m.] and chlorophyll *a* to chlorophyll *b* ratio in aboveground parts of grass mixtures (a, c – ECO and b, d –ROADSIDE) grown in Bialystok at Popieluszki, Hetmanska, Piastowska and Raginisa streets. Plants were harvested in June, August and October 2011

According to literature, ratio of chlorophyll *a* to chlorophyll *b* of higher plants is about 3. In our study, a much lower ratio of chlorophylls was obtained. Taking into account the date of harvest, the lowest ratio of chlorophyll *a* to *b* occurred in June and August, while in the grass collected in October higher ratio of chlorophylls was found (Fig. 1a–d). The reason for variations in chlorophyll *b* concentration was probably a dose of sewage sludge, which influence was more significant for chlorophyll *b* than for chlorophyll *a*. Probably, in the first months of research, plants were affected by stress caused by application of sewage sludge and month to month the plants have evolved adaptive mechanisms. According to Starck [40], changes in chlorophyll *a* and *b* in unfavorable conditions may be also a result of repair mechanisms, which could explain the low ratio of chlorophylls in August and higher in October. Many authors draws attention to heavy metals in sewage sludge, which in excessive amounts may adversely affect the plants [36, 41]. Moreover Sikorski [42] points out that the chlorophylls are considered to be the most sensitive vegetables pigments and heavy metals speed up changes chlorophylls concentration [43].

In the case of grass grown under control conditions, the average ratio of chlorophyll *a* to *b* was low, but in all cases, it was higher in comparison with the plants from fertilized plots (Fig. 1a–d). During ontogeny plants are exposed to various biotic and abiotic stressors. A stress causes certain plant reaction which consist to changing metabolic processes and as a result of its growth and development [44]. Pollution caused by transport in areas along a routes could be an additional stress factor that contributed to the low chlorophyll *a* to *b* ratio in plants collected from control plots in the firs months of study.

Conclusion

1. Sewage sludge soil amendment of urban lawns influenced plant nitrogen, potassium, chlorophyll *a* and chlorophyll *b* concentrations, the ratio of chlorophyll *a* to *b* the yield of dry matter.
2. Nitrogen concentration in the studied mixtures of lawn grasses increased proportionally with dose of sewage sludge. The highest concentration of this component in the grasses was when 15.0 kg $\cdot$ m^{-2} of sewage sludge was used. Accumulation of nitrogen in plants depended on the sampling time and location.
3. None of the experimental factors did influence significantly the concentration of phosphorus in lawn grass mixtures.
4. Potassium concentration in lawn grass mixtures was low in all variants of fertilization. Level of potassium in grasses depended on the dose of sewage sludge, mixtures of grasses and location.
5. Dry matter of investigated lawn grass mixtures was determined by the dose of sewage sludge, the time of sampling and location. The highest grass dry matter was from plots where the highest dose of sludge (15.0 kg $\cdot$ m^{-2}) was used.
6. Sludge fertilization influenced chlorophyll *a* and *b* concentration in the studied grasses; an increase of dose caused an increase in chlorophyll concentration.
7. The availability of main macronutrients for plants should be concidered taking into account not only dose of applied sewage sludge but also other environmental factors including impact of transport.

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WPŁYW OSADU ŚCIEKOWEGO NA PRODUKCJĘ BIOMASY I ZAWARTOŚĆ MAKROSKŁADNIKÓW ORAZ CHLOROFILU W MIESZANKACH TRAW

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Abstrakt: Celem podjętych badań było określenie wpływu różnych dawek komunalnego osadu ściekowego na przyrost biomasy części nadziemnych, a także na zawartość makroskładników oraz chlorofilu w mieszankach traw gazonowych. Założono cztery doświadczenia na trawnikach wzdłuż głównych ciągów komunikacyjnych Białegostoku: przy ul. Popiełuszki, Hetmańskiej, Raginisa i Piastowskiej. Czynnikami w doświadczeniu były trzy dawki osadu ściekowego: 0 (kontrola), 7,5 i 15 kg · m^{-2} oraz dwie mieszanki traw gazonowych: Eko i Roadside. Próbki części nadziemnych traw pobrano w trzech terminach: w czerwcu, sierpniu i październiku 2011 r., po czym oznaczono w nich: ilość biomasy części nadziemnych traw z 1 m^2, ogólne formy azotu, fosforu i potasu oraz określono zawartość chlorofilu *a* i *b*. Osad ściekowy wpłynął istotnie na akumulację N i K w trawach. Maksymalną średnią zawartość azotu (2,82 % s.m.) zaobserwowano w trawach z poletek z największą dawką osadu, z kolei potasu – w trawach z poletek z dawką osadu wynoszącą 7,5 kg · m^{-2}. Gromadzenie biomasy traw w okresie badań było różnicowane głównie przez ilość dawek osadu ściekowego oraz termin pobierania próbek. Średni sumaryczny plon suchej masy roślin dla trzech miesięcy badań (czerwiec, sierpień i październik) wynosił od 229,83 do 430,70 g · m^{-2}. Najlepsze efekty uzyskano przy zastosowaniu dawki osadu ściekowego wynoszącego 15 kg · m^{-2}. Termin zbioru oraz dawka osadu wpłynęły istotnie na zawartość chlorofilu *a* i *b* w badanych trawach. Średnie zawartości chlorofilu *a* w czerwcu, sierpniu i październiku wynosiły odpowiednio: 0,60; 0,64 i 0,54 mg · g^{-1} ś.m., z kolei chlorofilu *b*: 1,00; 0,94; 0,39 mg · g^{-1} ś.m. Stwierdzono niski średni stosunek chlorofilu *a* do *b* w badanych mieszankach traw, który wynosił od 0,54 w czerwcu do 1,82 w październiku dla mieszanki Eko oraz od 0,57 w czerwcu do 1,68 w październiku dla mieszanki Roadside. Rośliny z poletek kontrolnych wykazywały wyższy średni stosunek chlorofilu *a* do *b* w porównaniu do roślin z poletek użyźnionych osadem.

Słowa kluczowe: biomasa, trawy gazonowe, makroskładniki, chlorofil, osady ściekowe

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NITROGEN AND PHOSPHORUS LOADS IN THE RESTORED LAKE SAWAG

STAN ZANIECZYSZCZENIA RENATURYZOWANEGO JEZIORA SAWĄG ZWIĄZKAMI AZOTU I FOSFORU

Abstract: The aim of this study was to evaluate the ecological status of the restored Lake Sawag in the Olsztyn Lakeland. The analyzed water body was drained in the 19th century and converted into farmland. The former lake had an area of around 230 ha, and it was the largest drained water body in the Olsztyn Lakeland. The drained lake basin had been used as grassland until the 1990s when it was gradually filled with water due to the failure of outdated drainage systems. At present, Lake Sawag comprises three separate bodies of water with a combined area of 106 ha. Its catchment is used for agricultural purposes which, in view of the lake's small depth, poses a serious threat of degradation to the aquatic environment. The described study was conducted during four hydrological years of 2008 to 2011, and it covered three constituent sections of the contemporary Lake Sawag: northern (62 ha), central (14 ha) and southern (30 ha). Water samples were collected eight times in each year of the study, and they were analyzed to determine the concentrations of: nitrites(III), nitrates(V), ammonia nitrogen, total nitrogen, total phosphorus and dissolved phosphates. The following parameters were also measured: oxygen concentrations, pH, electrolytic conductivity, chlorophyll a and turbidity levels in water samples. The results of the above analysis point to low water quality in the restored lake. All sections of the studied water body were characterized by high electrolytic conductivity (average of 403 $\mu S \cdot cm^{-1}$), highly excessive phosphorus levels (0.30 $mg \cdot dm^{-3}$) and intensive phytoplankton blooms. The example of Lake Sawag indicates that although restoration projects generate numerous advantages for the ecosystem (protection of water resources, scenic value, fishing), they are susceptible to degradation and difficult to maintain in a satisfactory ecological condition.

Keywords: restored lake, rural catchment, nitrogen, phosphorus, eutrophication

Shallow (polymictic) lakes are the predominant type of water bodies found in the lake districts of northern Poland [1]. They differ from deep water bodies with regard to their functional attributes, in particular the absence of thermal stratification in the summer [2, 3]. Most shallow lakes are highly susceptible to degradation [3, 4]. The above results from internal factors (small depth and volume, contact with bottom deposits, resuspension of sediments due to near-bottom wave motion and activity of

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benthic organisms) as well as external influences (inflow of organic matter from the catchment) which contribute to eutrophication. Thermal stratification, a phenomenon encountered in deeper lakes in the summer, is not observed in shallow water bodies and, as a result, the entire water column of a shallow lake undergoes complete mixing. Bottom deposits are activated, and nutrients are exchanged between sediments and water. Shallow lakes are also susceptible to resuspension which enhances internal loading – the movement of biogenic substances from bottom deposits into water [5].

The functioning of shallow lakes is described by the theory of alternative stable states [6–8] in the light of which, an aquatic ecosystem may become permanently dominated by phytoplankton (stable state of turbid water) or macrophytes (state of clear water). Highly fertile lakes of the moderate climate zone are unlikely to be dominated by submerged macrophytes [3, 7]. A stable state of macrophyte domination can be achieved in degraded lakes only through radical restoration efforts that limit external load (biomanipulation, phosphorus inactivation) and break the predominance of phytoplankton in the ecosystem [9]. Measures which increase a lake's resistance to degradation, such as increasing water volume through water accumulation or ponding, may have a beneficial effect on the ecological status of shallow water bodies [3, 7]. In extreme cases, water accumulation can lead to the restoration of a dried water body, as in Lake Sawag. According to Scheffer [7], there is a general scarcity of published data about lakes that had existed as dry basins for long periods of time. Information about the underlying mechanisms and course of eutrophication in restored lakes is, therefore, vital from both scientific and practical points of view.

The objective of this study was to evaluate the ecological status of the restored Lake Sawag in the Olsztyn Lakeland. The analyzed water body had been drained and converted into grassland in the 19th century. The lake was partially restored relatively recently, therefore, the results of our study could provide valuable insights into the initiation of trophic processes in a "young" water body.

Materials and methods

The object of our study was Lake Sawag in the municipality of Swiatki in the Olsztyn Lakeland (53°58′36″ N, 20°18′51″ E). In the 19th century, the lake was drained and converted into meadows. Prior to the drainage project, Lake Sawag had a much higher water level and a surface area of around 230 ha (Fig. 1), rendering it the largest drained water body in the Olsztyn Lakeland [10]. The analyzed water body is marked as Lake Sawanna in 18th century maps, and prior to drainage in the 19th century, it was known as Lake Sawag or Legnowskie [11]. The drainage effort took place in 1870–1871, and it led to the lake's complete disappearance. The basin had been used as grassland (partially water-logged) until the 1990s when it was gradually filled with water due to the failure of outdated drainage systems.

According to reference data, the southern and central parts of the lake were restored in 1994–1995, and the northern part – around the year 2000. During the period of the study, the "new" Lake Sawag was a young body of water characterized by weakly developed aquatic vegetation and rush plants.

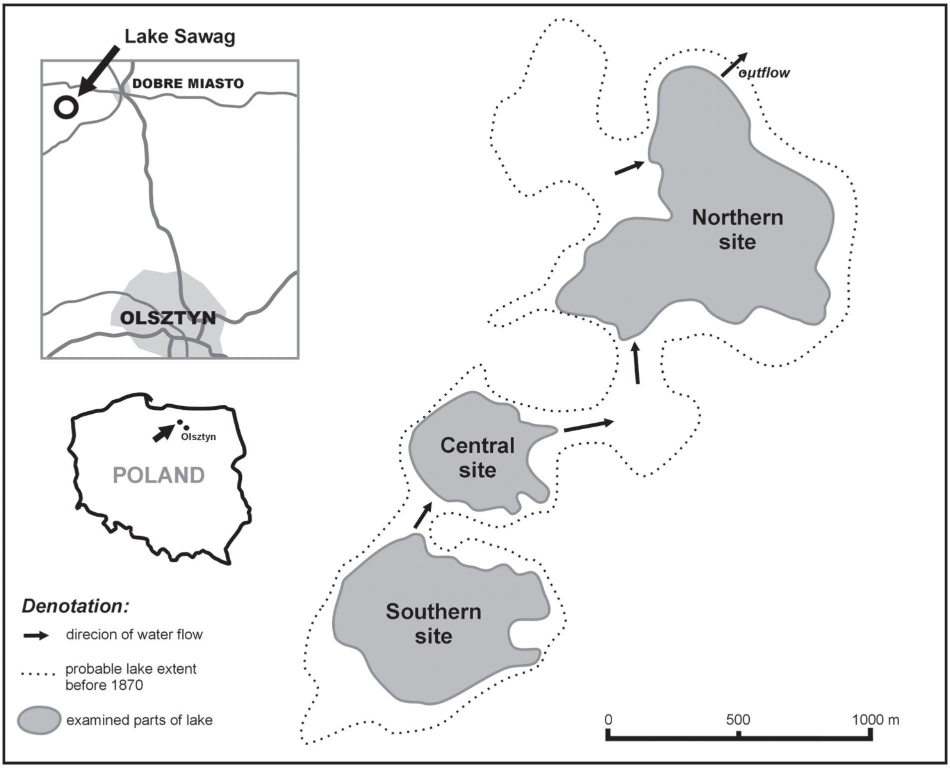

Fig. 1. Location of the analyzed site with a division into constituent sections (source: own study)

At present, Lake Sawąg has an area of 106 ha, and it comprises three distinct water bodies (Fig. 1) connected by a system of open ditches: the northern (62 ha), central (14 ha) and southern (30 ha) sections situated at the altitude of 109 (northern section) and 109.5 m above sea level (southern and central sections).

The catchment of the former lake has an area of 755 ha, 90 % of which is used for farming purposes. Partial catchments are separated into three parts which correspond to the three contemporary sections of the lake. Built-up areas cover 4.3 % of the catchment area of the northern section of the lake: they are the village of Legno with a population of 400 and a residential estate formerly administered by a State Agricultural Farm. In addition to surface runoffs, a small water course exiting the village and the estate is the main source of pollution in the analyzed lake. Village Legno and the northern section of the lake are separated by an additional body of water which constituted a separate site in the first years after the lake's restoration, but due to rising water levels, it was joined with the northern section of Lake Sawag. Forests cover 4 % of the catchment area, and they are limited to a cluster of trees in the central section of the lake and green belts along its shore. The layout of certain afforested fragments seems to reflect the lake's original shoreline before it was drained 140 years ago (Fig. 1).

The study was carried out in the course of four hydrological years of 2008 to 2011, and it covered three contemporary sections of Lake Sawag: northern, central and southern. Each year, water samples were collected eight times at equal time intervals – two samples in the spring, summer, fall and winter season. They were analyzed to determine the concentrations of: nitrites(III), nitrates(V), ammonia nitrogen, total nitrogen, total phosphorus and dissolved phosphates. All analyses were carried out in the laboratory of the Department of Land Improvement and Environmental Management at the University of Warmia and Mazury in Olsztyn, with the involvement of standard analytical methods. In-situ measurements were also performed to determine oxygen concentrations, pH, electrolytic conductivity, chlorophyll a and turbidity levels in water samples, with the use of the YSI 6600 multi-parameter probe.

Results

The results of evaluations carried out in 2008–2011 revealed a poor ecological status of Lake Sawag, in particular high phosphorus concentrations which are responsible for eutrophication. Selected water quality parameters (Table 1) were indicative of a disturbed ecosystem, but the average values of analyzed indicators remained relatively stable in successive years of the study. The lake was characterized by satisfactory oxygen concentrations with a distinctive rise in dissolved oxygen levels on a seasonal basis.

Table 1

Average values and standard deviation of selected water parameters in the southern, central and northern sections of Lake Sawag in 2008–2011

Site	Year	Parameter / Value (standard deviation)				
		Dissolved oxygen [%]	pH range	Conductivity $[\mu S \cdot cm^{-1}]$	Chlorophyll a $[\mu g \cdot dm^{-3}]$	Turbidity [NTU]
Southern	2008	90.4 (±10.5)	7.71–8.74	417 (±22.4)	34.9 (±20.5)	6.2 (±1.7)
	2009	109.4 (±24.2)	7.56–8.13	425 (±20.5)	29.9 (±10.1)	6.1 (±3.9)
	2010	103.2 (±21.7)	7.07–8.97	404 (±76.3)	21.5 (±16.3)	13.6 (±16.7)
	2011	100.1 (±22.1)	7.64–8.88	389 (±10.2)	24.3 (±13.7)	10.5 (±6.9)
	2008–2011	**100.8 (±20.5)**	**7.07–8.97**	**410 (±42.2)**	**27.8 (±15.8)**	**9.1 (±9.5)**
Central	2008	108 (±29.8)	7.75–8.83	386 (±23.8)	33.8 (±14.8)	6.9 (±4.6)
	2009	93.9 (±24.6)	7.53–8.18	413 (±25.2)	26.1 (±14.1)	5.4 (±4.1)
	2010	98.1 (±23.7)	7.14–9.00	412 (±57.9)	30.1 (±19.0)	7.9 (±5.9)
	2011	109.6 (±22.8)	7.72–8.92	396 (±19.1)	41.3 (±25.1)	6.0 (±2.4)
	2008–2011	**102.2 (±25.1)**	**7.14–9.00**	**402 (±35.7)**	**32.6 (±18.4)**	**6.6 (±4.4)**
Northern	2008	87.1 (±13.4)	7.85–8.76	428 (±26.9)	26.3 (±10.6)	7.8 (±9.2)
	2009	124.7 (±38.1)	7.61–8.15	382 (±44.1)	40.4 (±21.6)	11.6 (±9.3)
	2010	110.6 (±27.4)	7.25–8.86	377 (±76.0)	32.2 (±19.3)	14.5 (±16.6)
	2011	104.1 (±26.9)	7.79–8.74	395 (±21.8)	22.5 (±6.5)	5.4 (±1.3)
	2008–2011	**106.7 (±29.9)**	**7.25–8.86**	**396 (±49.8)**	**30.6 (±16.6)**	**10.0 (±10.8)**

Extreme oxygen concentrations reached 150 % in the southern section, 172 % in the central section and 200 % in the northern section of the lake. Oxygen saturation exceeded 65 % in all water samples, including in the winter. Winter anoxia, which is characteristic of excessively productive water bodies, was not observed due to large quantities of phytoplankton, including in the coldest months of the year.

Electrolytic conductivity remained fairly stable during the experimental period, and no significant variations were reported between the evaluated sections of the lake. Electrolytic conductivity values were generally high, which is usually the case in polymictic water bodies and catchment areas that are used for agricultural purposes. In line with the criteria for evaluating the quality of lake water [12], electrolytic conductivity exceeded the norm ($>350\ \mu S \cdot cm^{-1}$) in all sections of the water body and in all seasons. The average values throughout the period of the study ($410\ \mu S \cdot cm^{-1}$ in the southern section, $402\ \mu S \cdot cm^{-1}$ in the central section and $396\ \mu S \cdot cm^{-1}$ in the northern section) were significantly higher than those noted in Lake Nowe Wloki, a water body with a similar transformation history (it was reclaimed in the 19th century and restored in later periods). Twenty years after restoration, the average electrical conductivity in Lake Nowe Wloki was $233\ \mu S \cdot cm^{-1}$ [13].

Lake Sawag was characterized by high chlorophyll a levels which remained relatively stable during the four-year period of the study. Average chlorophyll a concentrations of $30\ \mu g \cdot dm^{-3}$ testify to high productivity levels. The values of the above parameter were similar in all sections of the water body, and they did not deviate significantly from average values in each season. Chlorophyll concentrations were also high under ice cover in the winter. Lake Sawąg has a stable phytoplankton community structure, with cyanobacteria as the predominant primary producers in the ecosystem. Water turbidity was high and stable in 2008, 2009 and 2011, whereas significantly higher turbidity levels were reported in 2010 (Table 1). In the summer of 2010, water temperature exceeded 25 °C and extensive cyanobacteria blooms contributed to the achievement of maximum turbidity values in all sections of the lake at 38.6 NTU in the southern section, 19.2 NTU in the central section and 42.9 NTU in the northern section of the water body. During that period, Secchi disc visibility in the northern section decreased considerably to 0.35 m.

Lake Sawag was moderately abundant in nitrogen compounds. Average total nitrogen concentrations insignificantly exceeded threshold values to reach $2.05\ mg \cdot dm^{-3}$ in the southern section, $2.13\ mg \cdot dm^{-3}$ in the central section and $2.44\ mg \cdot dm^{-3}$ in the northern section of the lake (Fig. 2). Clearly higher average nitrogen levels in the southern part could be attributed to the presence of built-up areas in the catchment area and the fact that it was the youngest section of the restored lake. In the summer and fall, high nitrogen concentrations were the result of intensive cyanobacteria blooms. In the above periods, nearly 90 % of nitrogen occurred in organic form. The organic form was also predominant in the remaining seasons, and the share of dissolved mineral forms did not exceed 20 % (Fig. 3). Average concentrations of mineral nitrogen reached $0.30\ mg \cdot dm^{-3}$ in the southern section, $0.34\ mg \cdot dm^{-3}$ in the central section and $0.31\ mg \cdot dm^{-3}$ in the northern section. Ammonia nitrogen accounted for 2/3 of the above values on average. Unlike phosphorus, moderate N-min levels (water quality class II) were also observed in the growing season. Similarly to Lake Nowe Wloki [14], the lowest mineral nitrogen concentrations were reported in the spring, but in Lake Sawag, mineral nitrogen levels were considerably lower throughout the year.

The phosphorus limits for waters not meeting quality standards (0.20 mg · dm^{-3}) were significantly exceeded in Lake Sawag. The average phosphorus concentrations

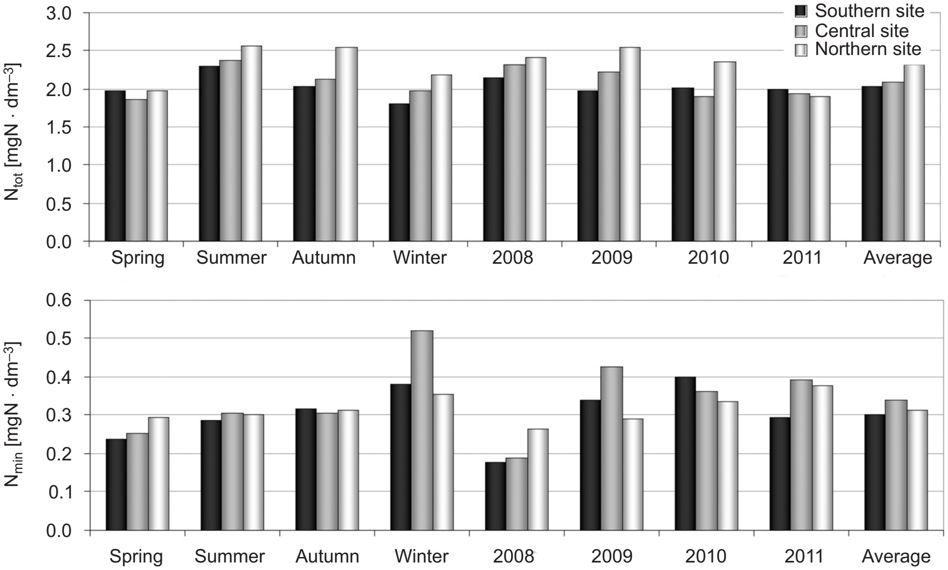

Fig. 2. Total nitrogen (N_{tot}) and mineral nitrogen (N_{min}) concentrations in three sections of Lake Sawag – seasonal, annual and average values for the entire period of the study (2008–2011)

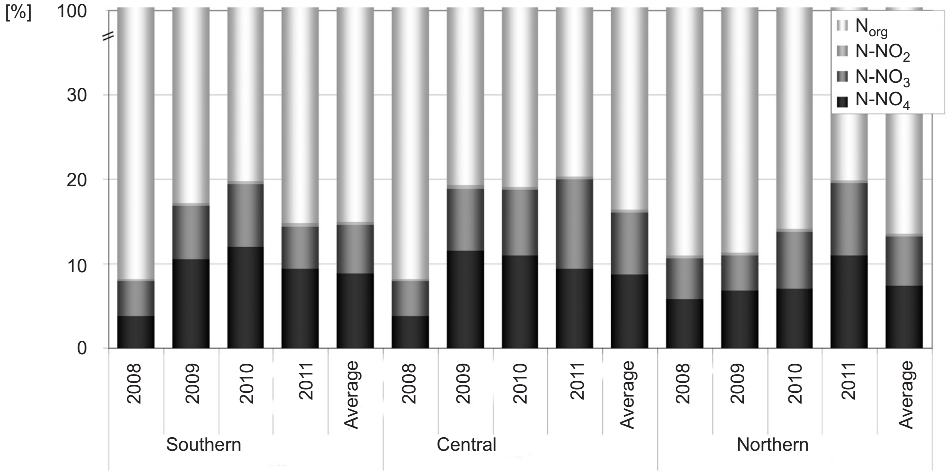

Fig. 3. Share of different nitrogen forms in the water of the studied sections of Lake Sawag in 2008–2011

over the period of the study reached 0.29 mg · dm^{-3} in the southern and northern sections and 0.31 mg · dm^{-3} in the central section (Fig. 4). Nearly 80 % of phosphorus occurred in organic form, but high phosphate levels were noted in the summer and fall. The above points to highly excessive amounts of phosphorus in circulation. As a result, primary production in the ecosystem was not nutrient (phosphorus) limited. If that were the case, the widespread growth of phytoplankton could have been prevented [7]. Average phosphorus levels were nearly 50 % higher in comparison with Lake Nowe Wloki [14], but unlike in the latter, very high phosphorus concentrations were maintained in Lake Sawag also in the fall. In the analyzed water body, excessive phosphorus content was probably the main factor preventing a natural improvement in the ecological status of the restored lake. According to research data [15], the maintenance of a clear water status requires phosphorus loads that do not exceed 0.10 mg · dm^{-3}. In Lake Sawag, the above level was more than twice higher in the spring and winter, and it reached nearly 0.40 mg · dm^{-3} in the summer and fall in all three sections of the water body (Fig. 4).

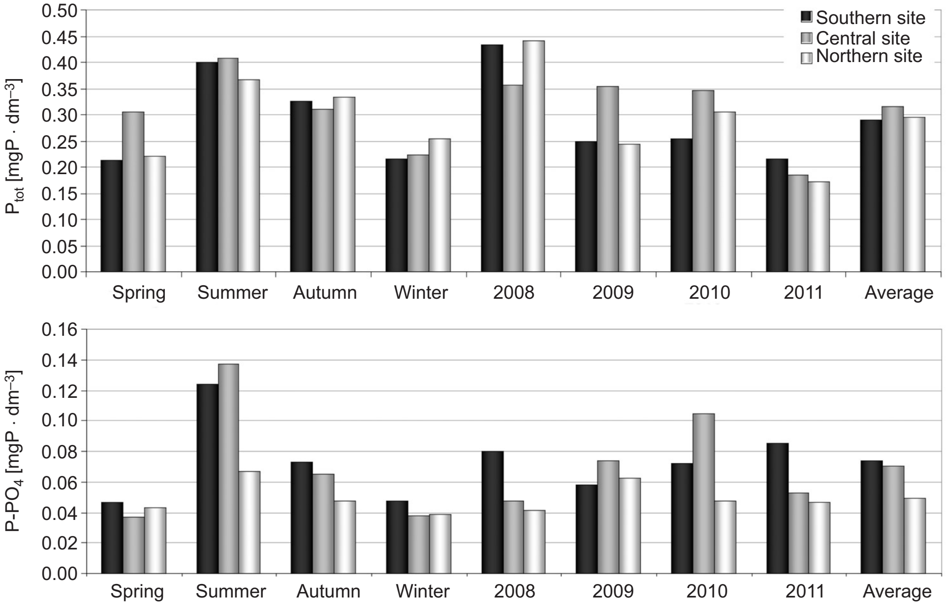

Fig. 4. Total phosphorus (P_{tot}) and phosphate ($P\text{-}PO_4$) concentrations in the water of the studied sections of Lake Sawag – seasonal, annual and average values for the entire period of the study (2008–2011)

Lake Sawag had remained dry for more than a century, and only around 50 % of its original area was restored. At the beginning of the study, it was a relatively young water body – the southern and central sections had existed for 12–13 years, and the northern section – for 7 years. The results of our assessment indicate that the major component of the restored ecosystem were phytoplankton communities and that macrophytes played a minor role as primary producers. High levels of phosphorus contributed to the stable growth of phytoplankton. Based on phosphorus concentrations in the experimental period, all three sections of the lake were classified as hypertrophic water bodies (Table 2). Trophy levels varied across different years of the study, excluding the smallest central section where phosphorus loads remained radically high throughout the entire experiment. Based on phytoplankton-related parameters (chlorophyll a concentrations and Secchi disk visibility), the sections of Lake Sawag were classified as eutrophic to polytrophic water bodies. With a steady supply of mineral phosphorus, the lake probably achieved a state of ecological balance in which primary production was inhibited by the limited availability of light. The above is characteristic of lakes with a stable turbid-water state.

Table 2

Trophy levels in the studied sections of Lake Sawag in 2008–2011:
southern (Sth), central (Ctr) and northern (Nth), based on [16];
trophy levels: E – eutrophic, P – polytrophic, H – hypertrophic (> 100 % threshold of polytrophy)

Site	Period	N_{tot} (Spring)		P_{tot} (Spring)		Chorophyll *a* – mean (Annual)		Chlorophyll *a* – max.		Secchi depth – mean (Annual)		Secchi depth – min	
		Value	State	Value	State	Value	State	Value	State	Value	State	Value	State
Sth	**Average 2008–11**	**1.97**	**P**	**0.21**	**H**	**27.8**	**P**	**51.9**	**E**	**1.09**	**E**	**0.67**	**P**
	2008	2.12	P	0.45	H	34.9	P	68.3	E	1.04	E	0.76	E
	2009	1.91	P	0.16	P	29.9	P	47.8	E	1.16	E	0.79	E
	2010	1.77	P	0.08	E	21.5	E	51.5	E	1.18	E	0.47	P
	2011	2.08	P	0.16	P	24.3	E	39.9	E	0.97	P	0.64	P
Ctr	**Average 2008–11**	**1.87**	**P**	**0.30**	**H**	**32.6**	**P**	**67.7**	**E**	**1.11**	**E**	**0.70**	**E/P**
	2008	2.02	P	0.44	H	33.8	P	64.0	E	1.05	E	0.58	P
	2009	1.48	E	0.24	H	26.1	P	46.6	E	1.21	E	0.73	E
	2010	1.88	P	0.33	H	30.1	P	68.7	E	1.09	E	0.57	P
	2011	2.09	P	0.21	H	41.3	P	91.4	P	1.09	E	0.92	E
Nth	**Average 2008–11**	**1.98**	**P**	**0.22**	**H**	**30.6**	**P**	**50.7**	**E**	**1.05**	**E**	**0.63**	**P**
	2008	2.05	P	0.38	H	26.3	P	47.4	E	1.17	E	0.59	P
	2009	1.60	P	0.14	P	40.4	P	72.1	E	0.90	P	0.58	P
	2010	2.27	P	0.18	P	32.2	P	54.9	E	1.02	E	0.37	P
	2011	2.01	P	0.18	P	22.5	E	28.5	E	1.12	E	0.97	E

An N : P supply ratio below threshold values (Fig. 5A) and a high average ratio of phosphorus to chlorophyll a concentrations (Fig. 5B) are also indicative of excessive phosphorus concentrations in Lake Sawag. It is assumed that a P : Chl ratio of 3 : 1 is the threshold value supporting a shift between stable states (phytoplankton and macrophyte) [6, 7]. In the analyzed lake, the above balance was significantly tipped in favor of phosphorus, and the average P : Chl ratio was determined at 8.64 : 1 (Fig. 3). After the first three years of the study, significant similarities in P : Chl ratio values were noted in the southern and central sections (9.8 : 1 and 9.7 : 1, respectively), whereas the share of phosphorus was lower in the northern section of the lake (6.9 : 1).

Following intensive phytoplankton blooms in 2011, the P : Chl ratio in the central section approximated the values noted in the northern part of the water body (Fig. 5B). The above change provides further evidence of excessive phosphorus levels in the ecosystem, pointing to a long-lasting steady state of phytoplankton in the lake.

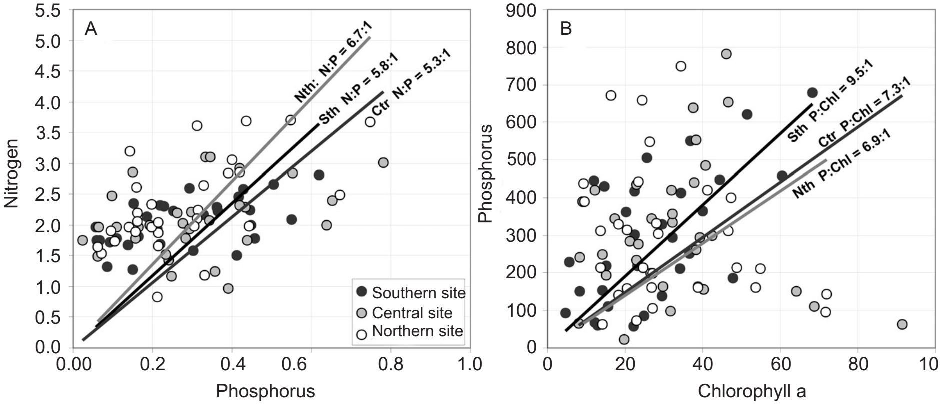

Fig. 5. Nitrogen to phosphorus ratio (A) and phosphorus to chlorophyll a ratio (B) in the studied sections of Lake Sawag, based on data acquired in 2008–2011

An improvement in the ecological status of shallow lakes is difficult to achieve because it requires a reduction in both external and internal sources of nutrient supply [3]. According to published data, the achievement of a clear-water state requires the elimination of algal blooms. Such a state occur in lakes where macrophytes, in particular submerged plants, act as primary producers. In Lake Sawag, phytoplankton communities, mostly cyanobacteria, were the predominant group of primary producers throughout the entire period of the study. Phytoplankton growth is the key contributor to turbidity, and this problem is very difficult to eliminate. Excessive proliferation of cyanobacteria was observed in the summer and fall, the above increased turbidity levels while chlorophyll a concentrations remained high and stable.

In shallow lakes, internal nutrient supply and phytoplankton blooms may neutralize the protective effects of reduced pollutant supply from external sources. The movement of biogenic substances from bottom deposits to water becomes the main supply mechanism for primary producers. Massive growth of phytoplankton additionally contributes to this process. The assimilation of biogenic substances, in particular phosphorus, leads to nutrient depletion, and the resulting deficit initiates the diffusion of additional sources from bottom deposits [17]. In Lake Sawag, those processes were additionally reinforced by an absence of land obstacles which would protect the lake from wind. The above leads to intensive wave motion which further contributes to sediment resuspension and inhibits lake colonization by vascular plants. Those negative effects could be somewhat alleviated by planting rows of trees along the shoreline which would act as barriers against external sources of pollution.

Restored lakes are a special example of shallow lake ecosystems [3]. Steady-state phytoplankton assemblages are likely to colonize a water body shortly after its restoration in a farmland. A high supply of biogenic substances from the catchment area and ecosystem hysteresis preserves the steady-state ecosystem [18]. The results of our study indicate that Lake Sawag has found itself in a "eutrophication" trap which will be difficult to escape in the course of its evolution. The lake's water level continues to rise, and an increase of approximately 0.5 m was noted during the four-year study. Rising water levels increase the lake's surface area and shift its shoreline. The noted changes suggest that the lake restoration process is likely to continue in the future, which should be regarded as a positive sign. Protective measures aiming to reduce the supply of organic matter from the catchment cannot be planned, however, until the lake's hydrological regime has been stabilized.

Conclusions

1. Lake Sawag, a recently restored water body that had remained dry for more than a century, was studied between 2008 and 2011. It was characterized by high trophy levels as well as high concentrations of chlorophyll a, phosphorus and nitrogen.
2. The analyzed ecosystem revealed symptoms of alternative steady-state phytoplankton growth with the predominance of cyanobacteria. In shallow, with an abundant supply of biogenic substances, the above may limit the effectiveness of protective measures aiming to reduce nutrient supply from the catchment.
3. The restoration of formerly dried lakes could improve the quality of water resources in catchment areas used for agricultural purposes. The example of Lake Sawag, the largest water body of the Olsztyn Lakeland dried in 19th century, indicates that restored lakes are highly susceptible to degradation. Excessive phosphorus concentrations seem to be the main obstacle to an improvement in the lake's ecosystem.

Acknowledgements

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STAN ZANIECZYSZCZENIA RENATURYZOWANEGO JEZIORA SAWĄG ZWIĄZKAMI AZOTU I FOSFORU

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Abstrakt: Celem pracy była ocena stanu przekształconego jeziora Sawąg, położonego na Pojezierzu Olsztyńskim. Obiekt należy do jezior, które w XIX wieku zostały osuszone z przeznaczeniem na grunty rolnicze. Wcześniej jezioro miało powierzchnię około 230 ha, co kwalifikuje je jako największe odwodnione jezioro Pojezierza Olsztyńskiego. Po osuszeniu teren zagłębienia utrzymywany był jako łąki aż do lat 90. XX w., kiedy zbiornik zaczął się stopniowo odtwarzać w wyniku pogorszenia się drożności urządzeń melioracyjnych. Obecnie jezioro Sawąg składa się z trzech oddzielnych akwenów o łącznej powierzchni 106 ha. Obiekt charakteryzuje rolniczym użytkowaniem zlewni, co przy niewielkiej głębokości zbiornika powoduje jego znaczne zagrożenie degradacją. Badania prowadzono w ciągu czterech lat hydrologicznych 2008–2011 i objęto nimi 3 akweny, z których współcześnie składa się jezioro Sawąg: północny (62 ha), centralny (14 ha) i południowy (30 ha). Próbki wody do badań pobierano 8-krotnie w każdym roku i oznaczano w nich: azotany(III), azotany(V), azot amonowy, azot ogólny oraz fosfor ogólny i fosforany rozpuszczone. Dodatkowo mierzono koncentrację tlenu, odczyn, przewodność elektrolityczną, chlorofil a i mętność. Badania wykazały, że stan jeziora Sawąg po przywróceniu zwierciadła wody był niekorzystny. Wszystkie akweny cechowały się wysoką przewodnością elektrolityczną (średnio 403 $\mu S \cdot cm^{-1}$) i ogromnym nadmiarem związków fosforu w ekosystemie (0.30 $mg \cdot dm^{-3}$), a przez to tendencją do intensywnych zakwitów fitoplanktonu. Przykład jeziora Sawąg wskazuje, że renaturyzacja dawnych jezior, obok wielu korzyści (ochrona zasobów wodnych, walory krajobrazowe, wędkarstwo i inne), przynosi również poważny problem utrzymania ich stanu ekologicznego.

Słowa kluczowe: renaturyzacja jezior, zlewnia rolnicza, azot, fosfor, eutrofizacja

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USE OF DIFFERENT EXTRACTION AGENTS TO PREDICT ZINC UPTAKE BY PLANTS

WYKORZYSTANIE RÓŻNYCH EKSTRAHENTÓW W CELU PROGNOZOWANIA POBIERANIA CYNKU PRZEZ ROŚLINY

Abstract: The main aim of this work was to compare different extraction agents in order to identify those which are able to give us most reliable data for assessment of soil zinc content and for prediction of possible contamination of crop. In order to compare several extraction methods and to identify the most suitable one for the zinc transfer into plant and to examine behaviour of high doses of a sludge heavily contaminated with zinc (almost 7 000 mg Zn $\cdot$ kg^{-1}), a two year pot experiment was established in vegetation hall in 2005. There were chosen five soils with different pH value (from extremely acidic to neutral) and planted with four crops – spinach, carrot, spring wheat and maize. But for control combination there were treatments with lower dose of sludge (equivalent of 5 Mg (tons) of dry matter per hectare) and high dose (equivalent of 25 Mg (tons) of dry matter per hectare for spinach and carrot and 50 Mg (tons) for wheat and maize). Following extraction agents were used for soil analyses – *Aqua regia*, 2 mol $HNO_3 \cdot dm^{-3}$, 0.43 mol $HNO_3 \cdot dm^{-3}$, Mehlich III, CAT, DTPA, $CaCl_2$, and NH_4NO_3. Correlations of soil zinc content measured with particular extracting agents and zinc content in plants were calculated.

The best correlations were found with quantity of Zn soluble in weakest extraction agents – $CaCl_2$ and NH_4NO_3. They correlated with themselves and with zinc content in plans but not with other agents. The rest of agents mostly correlated among 0.43 mol $HNO_3 \cdot dm^{-3}$, Mehlich III, CAT and DTPA and between *Aqua regia* and 2 mol $HNO_3 \cdot dm^{-3}$. There were quite tight correlations between soil pH and zinc content in plants confirming that pH is a crucial factor for zinc soil mobility. It implies that knowledge of soil pH and (even) pseudo total zinc content can serve as a sufficient source of information about probable zinc status in the soil. Mehlich III, which is in the Czech Republic widely used for the Agrochemical Soil Testing (evaluation of P, K, Ca and Mg status of soil) can be used as a good screening tool (and perhaps for other microelements). Such use would provide a large scale of data without additional costs.

Keywords: zinc, extraction agents, availability

Zinc with its special position is one of the most important micronutrients, however, it can be also considered to be a contaminant. It depends on the situation in the soil. Low

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content of zinc combined with high pH can result in zinc deficiency. To the contrary, high zinc soil concentration and low pH can cause symptoms of toxicity or endanger the quality of a crop. For prediction of these effects we need some reliable tools, which can be represented by extraction agents of different strength and composition. The key requirement is that such extraction agent should allow predict the zinc content in plant based on its content in soil as precisely as possible. Stability under different soil conditions or low price of analysis can be advantage.

The main aim of this work was to compare different extraction agents in order to identify those which are able to give us most reliable data for assessment of soil zinc content and for prediction of possible contamination of crop.

Material and methods

In order to compare several extraction methods and to identify the most suitable one for the zinc transfer into plant and to examine behaviour of high doses of a sludge heavily contaminated with zinc (almost 7000 mg Zn $\cdot$ kg^{-1}), a two year pot experiment was established in vegetation hall in 2005.

There were chosen five soils (Sudice, Budisov, Netin, Ricky and Orechov) with different pH value, from extremely acidic to neutral (Table 1) and planted with four crops – spinach, carrot (after spinach harvest, in the same pot), spring wheat and maize. There was no crop rotation so for example wheat was followed by wheat etc. The only exceptions were spinach and carrot, which were planted in the same pot.

Table 1

Input parameters of soils

Soil	pH	P	K	Ca	Mg	Zn extracted with 2 mol $HNO_3 \cdot dm^{-3}$
		[mg $\cdot$ kg^{-1}]				
Sudice	4.4	127	209	987	103	22.9
Netin	5.5	120	283	1130	100	21.2
Budisov	4.9	225	157	1480	131	21.2
Ricky	6.2	50	133	2660	297	35.0
Orechov	7.1	393	798	5080	433	49.6

There were three combination, control and two doses of sludge. Each combination was repeated six times.

Sludge originated in wastewater treatment Modrice was dried and lime treated, its pH/$CaCl_2$ was 7.5 and moisture content 11.9 %. Its composition is presented in Table 2.

But for control combination there were treatments with lower dose of sludge (equivalent of 5 Mg (tons) of dry matter per hectare – 20.75 g $\cdot$ pot^{-1}) and high dose (equivalent of 25 Mg (tons) of dry matter per hectare for spinach and carrot – 103.75 g $\cdot$ pot^{-1} and 50 Mg (tons) for wheat and maize – 207.5 g $\cdot$ pot^{-1}).

Table 2

Chemical composition of sludge

Elements	Content [mg · kg^{-1} d.m.]				
Nutrients	P	K	Mg	Ca	Na
	20900	2260	4060	49400	565
Trace elements	As	Cd	Cr	Cu	Hg
	6.5	4.1	129	347	3.8
	Pb	Zn	Mo	Ni	Al
	242	6810	6.2	85.5	12800
	Be	Co	Fe	Mn	V
	0.6	13	51800	452	35.1

Fertilizing was performed before sowing. Nitrogen was applied to all pots (0.43 g · pot^{-1} for spinach and carrot and 0.85 g · pot^{-1} for wheat and maize) in urea form and soil from Ricky was fertilized also with phosphorus (0.5 g · pot^{-1} spinach, carrot and wheat and 0.62 g · pot^{-1} for maize) as a superphosphate approximately 7 cm below the soil surface.

Table 3

Factors of trial

Factor	Level of factor	Factor	Level of factor
Soil origin	Sudice	Crop	spinach/carrot
	Budisov		wheat
	Netin		maize
	Ricky		
	Orechov	Sludge dose	control
Year	2005		sludge I
	2006		sludge II

Pots were filled with 8 kg of soil. Deionised water was used for irrigation. After sprouting plants were singled to final number of 26 for spinach and wheat, 4 for maize and 12 for carrot.

Soil samples were taken after harvest separately from each pot. There was no sampling after the last harvest.

Following analyses were performed:

– pH/$CaCl_2$,

– content of Zn extracted with: *Aqua regia*, 2 mol HNO_3 · dm^{-3}, 0.43 mol HNO_3 · dm^{-3}, Mehlich III, CAT, DTPA, $CaCl_2$, NH_4NO_3.

Procedures of used extraction methods were as follows:

– *Aqua regia* – soil sample was extracted by hot mixture of hydrochloric acid and nitric acid (3:1, v/v; nitric acid c = 14.4 mol · dm^{-3}, hydrochloric acid c = 11.7 mol · dm^{-3}) and was regarded as total zinc content;

– 2 M HNO_3 – soil sample was extracted by nitric acid at room temperature with concentration of 2 mol HNO_3 · dm^{-3};

Table 4

Zinc content in soils in 2005 (average of all pots)

Locality	Zinc content in extract [mg · kg^{-1}]											
	Aqua regia			2 M HNO_3			0.43 M HNO_3			Mehlich III		
	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II
Sudice	42.9	49.3	91.5	22.4	28.8	73.5	12.2	17.1	56.1	7.8	11.7	41.7
Budisov	48.2	55.2	113.0	20.5	27.4	90.8	8.1	15.1	70.9	4.2	9.0	46.5
Netin	53.5	59.9	101.4	20.1	26.1	65.5	6.9	11.8	48.1	4.6	8.5	32.8
Ricky	62.0	65.5	111.7	31.7	45.5	87.0	20.7	27.4	67.9	12.0	15.0	43.3
Orechov	89.1	96.3	131.1	41.5	47.8	89.8	27.2	33.3	69.7	16.5	20.5	43.6
Locality	Zinc content in extract [mg · kg^{-1}]											
	CAT			DTPA			$CaCl_2$			NH_4NO_3		
	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II
Sudice	7.2	8.3	27.1	4.9	7.3	24.7	3.4	4.9	13.9	3.8	5.4	17.4
Budisov	7.0	7.1	27.8	2.3	5.1	28.2	3.0	3.0	6.3	1.1	2.0	6.9
Netin	7.0	7.5	22.7	2.7	5.1	21.0	3.0	3.0	3.3	0.9	1.1	2.8
Ricky	8.3	9.5	23.3	7.8	10.3	27.0	3.0	3.0	3.2	0.9	1.0	2.8
Orechov	11.5	14.5	32.9	6.7	8.9	24.6	3.0	3.0	3.0	0.9	0.9	0.9

Table 5

Relative zinc content in soils in 2005 (average of all pots) – *Aqua regia* as 100 %

Locality	[%]											
	Aqua regia			2 M HNO_3			0.43 M HNO_3			Mehlich III		
	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II
Sudice	100.0	100.0	100.0	52.1	58.4	80.4	28.5	34.7	61.3	18.3	23.7	45.6
Budisov	100.0	100.0	100.0	42.5	49.6	80.4	16.7	27.4	62.8	8.7	16.3	41.2
Netin	100.0	100.0	100.0	37.5	43.6	64.5	12.8	19.7	47.4	8.5	14.2	32.3
Ricky	100.0	100.0	100.0	51.1	69.4	77.9	33.4	41.8	60.8	19.3	22.8	38.7
Orechov	100.0	100.0	100.0	46.6	49.6	68.5	30.5	34.6	53.1	18.5	21.3	33.3

Locality	[%]											
	CAT			DTPA			$CaCl_2$			NH_4NO_3		
	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II
Sudice	16.7	16.9	29.7	11.3	14.7	27.0	7.8	9.9	15.2	8.7	11.0	19.0
Budisov	14.5	12.9	24.6	4.8	9.2	25.0	6.2	5.4	5.6	2.2	3.6	6.1
Netin	13.1	12.6	22.4	5.1	8.4	20.7	5.6	5.0	3.2	1.7	1.8	2.7
Ricky	13.4	14.5	20.8	12.6	15.8	24.2	4.8	4.6	2.8	1.5	1.5	2.5
Orechov	12.9	15.0	25.1	7.5	9.3	18.8	3.4	3.1	2.3	1.0	0.9	0.7

Table 6

Zinc content in soils in 2006 (average of all pots)

Locality	Zinc content in extract [mg · kg^{-1}]											
	Aqua regia			2 M HNO_3			0.43 M HNO_3			Mehlich III		
	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II
Sudice	45.4	54.2	109.3	22.1	30.3	82.9	11.1	18.6	73.2	6.8	11.9	42.9
Budisov	48.3	54.9	112.7	21.1	29.5	91.2	8.3	14.3	67.5	4.2	9.0	35.2
Netin	57.2	63.7	116.0	21.1	28.4	74.3	6.5	14.1	54.0	4.5	7.5	31.7
Ricky	60.3	69.7	124.9	31.2	40.8	93.3	19.4	27.9	75.0	10.5	15.1	39.6
Orechov	90.2	98.9	168.9	41.4	50.3	119.8	27.8	37.4	101.7	15.7	19.3	52.3

Locality	Zinc content in extract [mg · kg^{-1}]											
	CAT			DTPA			$CaCl_2$			NH_4NO_3		
	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II
Sudice	7.0	9.8	38.8	6.1	13.0	43.4	3.5	6.0	18.9	6.1	7.5	24.5
Budisov	7.0	7.0	32.9	2.5	5.7	40.2	3.0	3.0	9.6	1.0	3.0	13.2
Netin	7.0	7.0	28.1	3.1	5.1	30.7	3.0	3.0	4.6	0.9	1.2	5.4
Ricky	9.3	13.6	38.8	9.4	14.0	38.4	3.0	3.0	4.8	1.2	1.5	6.2
Orechov	10.8	14.1	41.5	6.8	8.8	29.9	3.0	3.0	3.0	0.9	0.9	0.9

Table 7

Relative zinc content in soils in 2006 (average of all pots) – *Aqua regia* as 100 %

Locality	[%]											
	Aqua regia			2 M HNO_3			0.43 M HNO_3			Mehlich III		
	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II
Sudice	100.0	100.0	100.0	48.8	56.0	75.8	24.4	34.4	67.0	14.9	21.9	39.2
Budisov	100.0	100.0	100.0	43.7	53.7	81.0	17.2	26.0	59.9	8.8	16.5	31.2
Netin	100.0	100.0	100.0	36.8	44.6	64.0	11.4	22.1	46.5	7.9	11.8	27.3
Ricky	100.0	100.0	100.0	51.8	58.6	74.7	32.1	40.1	60.1	17.3	21.7	31.7
Orechov	100.0	100.0	100.0	45.8	50.8	70.9	30.8	37.8	60.2	17.4	19.5	31.0
Locality	[%]											
	CAT			DTPA			$CaCl_2$			NH_4NO_3		
	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II	0	Slud I	Slud II
Sudice	15.4	18.1	35.5	13.4	24.0	39.7	7.7	11.0	17.3	13.4	13.8	22.4
Budisov	14.5	12.8	29.2	5.1	10.4	35.7	6.2	5.5	8.5	2.1	5.5	11.7
Netin	12.2	11.0	24.2	5.4	8.0	26.5	5.2	4.7	4.0	1.6	1.9	4.7
Ricky	15.4	19.5	31.1	15.6	20.0	30.7	5.0	4.3	3.8	2.0	2.2	5.0
Orechov	11.9	14.3	24.5	7.5	8.9	17.7	3.3	3.0	1.8	1.0	0.9	0.5

– 0.43 M HNO_3 – soil sample was extracted by nitric acid at room temperature with concentration of 0.43 mol $HNO_3 \cdot dm^{-3}$;

– Mehlich III – soil was extracted by acidic solution containing ammonium fluoride, ammonium nitrate, acetic acid, nitric acid and EDTA (*ethylenediaminetetraacetic acid*) in room temperature;

– CAT – soil was extracted by solution containing in 1 dm^3 14.7 g of $CaCl_2 \cdot 2\ H_2O$ and 7.88 g DTPA (*diethylenetriaminopentaacetic acid*), for extraction was this solution ten times diluted, room temperature;

– DTPA – extraction was performed in soil – DTPA solution ratio 1 : 2 (m/v) in exactly defined conditions with solution containing 0.1 mol $\cdot$ dm^{-3} triethanolamine, 0.01 mol $\cdot$ dm^{-3} calcium chloride and 0.005 mol $\cdot$ dm^{-3} DTPA at room temperature;

– $CaCl_2$ – solution of calcium chloride 0.01 mol $CaCl_2 \cdot dm^{-3}$ in room temperature;

– NH_4NO_3 – solution of ammonium nitrate 1 mol $NH_4NO_3 \cdot dm^{-3}$ in room temperature.

Final measurement in *Aqua regia* extract was performed by ICP-OES and in the rest extracts by AAS.

Concerning the plant material shoot biomass of spinach and maize was analysed, root of carrot and straw and grain of wheat. Samples were mineralised on a dry way in muffle furnace. Ash was dissolved in diluted nitric acid and zinc content was measured using ICP-OES.

Correlations of soil zinc content measured with particular extracting agents and zinc content in plants were calculated. Data was processed using STATISTICA 8. Correlations were evaluated using Pearson's correlation test.

Results and discussion

Comparison of extraction agents

On combination sludge II was observed increase in zinc content in *Aqua regia* extract in 2006. This can be partly explained by ongoing mineralisation of sludge. However, increase is not in line with theoretical increase based on amount of zinc applied, which is 14.7 mg $\cdot$ kg^{-1} for 5 Mg (tons), 73.2 mg $\cdot$ kg^{-1} for 25 Mg (tons) and 146.5 mg $\cdot$ kg^{-1} for 50 Mg (tons) of sludge. This "disappearing" of zinc was reported also in other works [1].

This increase in second year was not so apparent in other extraction agents. For calcium chloride and ammonium nitrate we observed clear dependence between soil pH and extracted zinc quantity. This is in accordance with other sources and furthermore those report that such differences (between extremely acidic and neutral soils) can be tens of percent [2].

In 2005 2 mol $HNO_3 \cdot dm^{-3}$ yielded on control up to 53 % of zinc extracted with *Aqua regia*, one year after up to 50 %, on sludge II up to 85 % and 80 %, respectively. Weaker concentration of nitric acid extracted up to 35 % and 30 % of total zinc content on control and on sludge II up to 66 % in both years. Mehlich III provided 20 % and 17 % of zinc extracted with *Aqua regia* on control and 42 % and 36 % on sludge II.

CAT yielded 17 % and 13 % of total zinc content on control, and on sludge II 34 % and 32 %, respectively. DTPA dissolved 11 % and 13 % of zinc extracted with *Aqua regia* on control and 27 % and 40 % on sludge II. $CaCl_2$ on control extracted 8 % and 7 %, and 18 % and 15 % of total zinc content on sludge II. Finally NH_4NO_3 dissolved 13 % and 9 % of zinc quantity extracted with *Aqua regia* on control, and on sludge II 22 % and 21 %. This illustrates the fact that applied zinc was quite mobile. If we compare our results with other sources it is obvious that in our case weak extraction agents extracted pretty high percentages of total content. In a study comparing different extractions from soils after sludge application was reported that $NaNO_3$ (which is comparable with NH_4NO_3) extracted around 1 % of zinc extracted by *Aqua regia*, $CaCl_2$ even only 0.3 % [3]. Other work offers very similar results especially for 2 mol $HNO_3 \cdot dm^{-3}$. Little bit higher results assigns to DTPA (8 %) and also to weak agents as NH_4NO_3 and $CaCl_2$, but also highlights the fact that in case of anthropogenic contamination contents assessed by weak extraction agents can easily exceed 10 % of total content [2]. In neutral soil (pH 7) $CaCl_2$ extracted only 0.05 % of total zinc content after long term application [4]. In contrary, another work reports $CaCl_2$ extracting 42 % of total zinc content many years after sludge application [5]. These results demonstrate fundamental influence of soil properties on zinc mobility and also illustrate complexity of this issue. It is also interesting to confront with conclusions of Slovak study which designates critical zinc content extracted by ammonium nitrate as 2 mg $\cdot$ kg^{-1} soil [6]. Our results indicate that such value could be too strict.

Correlations between extraction agents

All described correlations are statistically significant on a level $p < 0.05$. All localities and sludge combinations were evaluated.

There were only slight differences between years 2005 and 2006. There was an important finding that extraction agents as per their zinc extraction ability created in fact 4 groups according to their common correlations:

- *Aqua regia* and 2 mol $HNO_3 \cdot dm^{-3}$,
- 0.43 mol $HNO_3 \cdot dm^{-3}$, Mehlich III and CAT,
- DTPA,
- $CaCl_2$ and NH_4NO_3.

Correlations out of these groups exist, however, practically only between first two groups. Similar findings can be found in literature. It was quite surprising that DTPA became very isolated, there were hardly few correlations with stronger agents and even no with weaker used for zinc extraction. The only few correlations were found with Mehlich III and CAT. Both weakest agents correlated only with each other. Tight correlations of zinc quantity dissolved in $CaCl_2$ and NH_4NO_3 and additionally their relation to pH of soil are confirmed in other studies [7].

Correlations between plants and soils zinc content

Zinc content in spinach biomass was practically the only with correlations with one of stronger agents, particularly with DTPA. The relatively strong correlation was found

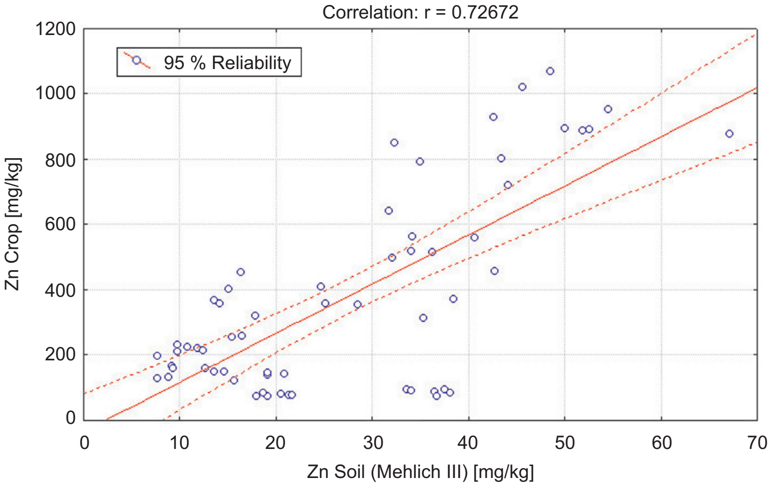

Fig. 1. Correlation between zinc content in soil (Mehlich III) on sludge I+II combinations and zinc content in spinach (2006)

between zinc extracted by Mehlich III from soils of all experimental objects and its spinach content (Fig. 1). The rest of plants (respectively their zinc content) correlated only with quantity of this metal extracted by NH_4NO_3 and $CaCl_2$. And ammonium nitrate provides pretty stronger correlations. We cannot omit the role of soil pH which is, however, stronger with separated combinations and especially under normal conditions represented by control (zero treatment) or lower sludge dose. We can state that soil pH is better tool for zinc uptake prediction than strong and medium strong extraction agents. This ability is mentioned in literature to [8]. This option for zinc uptake prediction is limited under more extreme conditions.

Generally speaking this is due to higher mobility of zinc in low soil pH and these mobile forms are extracted by weak agents. It is interesting to observe behaviour of DTPA. This agent created its own “group” and we can agree upon the fact that this agent fulfils just its original intention – to assess the nutrition level of zinc in soil. However, it fails if used for uptake prediction.

Detailed testing revealed no correlations (even with weak agents) for soil from Orechov, which has quite high pH value. This effect is confirmed by other sources to [9].

According to our expectations there were no correlations with strong extraction agents ability to zinc dissolving. This is supported by more studies [7], even though there exist also different conclusions, which demonstrate correlations with strong agents such as 2 mol $HNO_3 \cdot dm^{-3}$ [10, 11]. However, this is the case in which nitric acid correlates also with ammonium nitrate and it was found under natural conditions [11].

As the most appropriate extraction agent for zinc uptake prediction we considered ammonium nitrate. It is recommended in other studies, often together with calcium chloride [7]. It is important to mention that even this agent (NH_4NO_3) was not able to predict all increased contents of zinc in plants. On the contrary, even use of some of stronger agents (0.43 mol $HNO_3 \cdot dm^{-3}$, CAT, Mehlich III) in combination of knowledge of soil pH can be sufficient clue to predict possible risk of plant contamination and probably even phytotoxicity of zinc. Extreme soil condition represented by very low pH and very high concentrations of zinc can complicate use of extraction methods for uptake prediction. In that case the only reliable method for evaluation of contamination is analysis of plant material.

Conclusions

All used extraction agents were able to identify differences in zinc content of different combinations including the fact that sludge applied was released rapidly. Amount of applied zinc was higher than revealed by *Aqua regia*, part of this zinc remained undetected. Soil of high quality with neutral pH was able to immobilise applied zinc and protect crops even against very high level of contamination. On contrary, soils with low pH are not able to eliminate even low quantities of zinc and high uptake of zinc occurs. There are strong correlations of zinc content dissolved in *Aqua regia* and 2 mol $HNO_3 \cdot dm^{-3}$. Correlations of the same strength were detected between 0.43 mol $HNO_3 \cdot dm^{-3}$, Mehlich III and CAT, with some correlations with *Aqua regia* and 2 mol $HNO_3 \cdot dm^{-3}$. Zinc content in DTPA leach was hardly ever correlated with zinc in other extracts. Very strong correlations were found between zinc content in NH_4NO_3 and $CaCl_2$ extracts, but its amount soluble in these agents did not correlate with the rest. Contents of zinc in NH_4NO_3 and $CaCl_2$ extracts were in a good accordance with soil pH. Extraction with NH_4NO_3 shown the best correlation with plant zinc, a bit worse was $CaCl_2$. There were good results for soil pH and plant zinc for controls and lower sludge doses. DTPA was not applicable for prediction of elevated uptake. Strong agents in combination with soil pH value can offer very good information on possible risk of excessive plant uptake. Mehlich III which is used for assessment of soil nutrient status in the Czech Republic could be used as an appropriate extraction agent for screening of soil zinc (and perhaps other microelements) content.

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WYKORZYSTANIE RÓŻNYCH EKSTRAHENTÓW W CELU PROGNOZOWANIA POBIERANIA CYNKU PRZEZ ROŚLINY

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Abstrakt: Celem pracy było porównanie różnych ekstrahentów w celu identyfikacji tego, dzięki któremu będzie można uzyskać najbardziej rzetelne dane dla oceny zawartości cynku w glebie i prognozowania możliwości zanieczyszczenia roślin. W celu porównania kilku metod ekstrakcji i rozpoznania najbardziej odpowiadającej pobieraniu cynku przez rośliny oraz zbadania zachowania się dużych dawek osadów silnie zanieczyszczonych cynkiem (prawie 7 000 mg Zn $\cdot$ kg^{-1}), w 2005 r. założono dwuletnie doświadczenie wazonowe w hali wegetacyjnej. Wybrano pięć gleb o różnej wartości pH (od bardzo kwaśnych do obojętnych) i uprawiano pięć gatunków roślin – szpinak, marchew, pszenicę jarą i kukurydzę. Kombinacją kontrolną były obiekty z mniejszą dawką osadu (równoważną 5 Mg (tonom) suchej masy na 1 ha) i wysoką dawką (równoważną 25 Mg (tonom) suchej masy na 1 ha pod szpinak i marchew oraz 50 Mg (tonom) pod pszenicę jarą i kukurydzę). W badaniach użyto następujące ekstrahenty: woda królewska, 2 mol $HNO_3 \cdot dm^{-3}$, 0,43 mol $HNO_3 \cdot dm^{-3}$, Mehlich III, CAT, DTPA, $CaCl_2$ i NH_4NO_3. Obliczono współczynniki korelacji pomiędzy ilością cynku ekstrahowanego z gleby przez poszczególne ekstrahenty a zawartością cynku w roślinach.

Stwierdzono najsilniejszą korelację pomiędzy ilością cynku rozpuszczalnego w najsłabszym ekstrahentach – $CaCl_2$ i NH_4NO_3. Ilości te były skorelowane ze sobą oraz z zawartością cynku w roślinach, ale nie z ilością cynku rozpuszczalnego w innych ekstrahentach. Ilości cynku ekstrahowane przez pozostałe odczynniki ekstrakcyjne: 0,43 mol $HNO_3 \cdot dm^{-3}$, Mehlich III, CAT i DTPA, a także ekstrahowane wodą królewską i 2 mol $HNO_3 \cdot dm^{-3}$ były najczęściej skorelowane ze sobą. Stwierdzono dość ścisłe korelacje między pH gleby a zawartością cynku w roślinach potwierdzające, że pH jest kluczowym czynnikiem mającym wpływ na mobilność cynku w glebie. Oznacza to, że znajomość pH gleby i (nawet) zbliżonej do całkowitej zawartości cynku w glebie może służyć jako wystarczające źródło informacji o możliwym statusie cynku w glebie. Odczynnik Mehlich III, który jest szeroko stosowany w Czeskiej Republice w badaniach chemiczno-rolniczych (oceniających stan P, K, Ca i Mg w glebie), może być stosowany jako dobre narzędzie do badań przesiewowych (być może też do innych mikroelementów). Takie jego zastosowanie zapewni dużą liczbę danych bez dodatkowych kosztów.

Słowa kluczowe: cynk, ekstrahenty, przyswajalność

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ZINC, COPPER AND NICKEL IN SEQUENTIAL EXTRACTED FRACTIONS IN BOTTOM SEDIMENTS

CYNK, MIEDŹ I NIKIEL W SEKWENCYJNIE WYDZIELONYCH FRAKCJACH Z OSADÓW DENNYCH

Abstract: The total content of Zn, Cu, Ni, and their contribution in exchangeable (F1), reducible (F2), oxidizable (F3), and residual (F4) fractions separated by the sequential extraction procedure according to The European Union's Standards, Measurements, and Testing program (formerly BCR), in bottom sediments were determined. Samples were collected from bottom sediments surface layer (0–10 cm) of the "Row Strzala" canal that disposes reclaimed wastewaters from municipal sewage treatment plant in Siedlce and storm sewage system, to Liwiec river, as well as in the river, upstream and downstream of the canal estuary, located on the Siedlce Upland, in the eastern part of Mazovia province. The mean contents of tested heavy metals in surface layers of bottom sediments can be lined up in following decreasing sequence [$mg \cdot kg^{-1}$]: Zn (69.1) > Cu (5.81) > Ni (3.95). Higher total contents of Zn, Cu, and Ni were recorded in bottom sediments from canal rather than river. More studied metals were recorded in material collected from points near sewage treatment plant, while less at the point localized above its estuary to Liwiec river. Sediments from studied flows are counted to the 1st class – not contaminated sediments. The mean percentage contribution of Zn, Cu, and Ni in separated fractions, in relation to their total contents, can be arranged in the following decreasing series: for Zn: F2 (53.6) > F3 (21.0) > F4 (15.3) > F1 (10.2); for Cu: F3 (50.4) > F4 (25.7) > F2 (15.0) > F1 (8.90); for Ni: F4 (39.6) > F3 (26.6) > F2 (20.2) > F1 (13.6). Mobility of metals in exchangeable fraction (F1) in the investigated sediments can be lined up in following decreasing sequence Ni > Zn > Cu. Statistical processing revealed significant influence of selected properties of studied bottom sediments (sediments reaction, content of organic carbon compounds, value of cation exchange capacity, clay fraction – $\varnothing < 0.002$ mm) on zinc, copper and nickel speciation.

Keywords: bottom sediments, fraction of Zn, Cu, Ni, "Row Strzala" canal, Liwiec river

Bottom sediments are an important part of the aquatic environment. They form a habitat for plants and animals which is rich in nutrients and which plays an important role in the regulation of matter and energy circulation in the environment. Sediments in

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the surface water are formed as a result of sedimentation on the bottoms of watercourses of allochthonous material originating outside the sedimentation area (gravel, sand, silt, mineral and organic suspensions) and autochthonous material formed in the sedimentation area (depositing organic and inorganic substances, as well as decaying plant and animals remnants). Heavy metals are commonly regarded as particularly noxious and hazardous to the natural environment, frequently causing its pollution. When introduced to surface waters, they accumulate in bottom deposits, where their content is higher than in water. The intensity of element migration in the ecosystem is affected by geochemical, physicochemical, climatic and biological factors. The chemical composition of bottom sediments in watercourses depends on the geological structure of the drainage basin, the natural of land use around it and pollutants which enter surface waters (industrial and household sewage and surface runoff from agricultural land). The metal content in bottom deposits is an important indicator of the geochemical quality of an aquatic ecosystem and it provides important information on the anthropopressure on aquatic environment [1–6].

The total content of heavy metals in bottom deposits comprises their various fractions (species) with varying properties which take part in many processes in the environment, typical of a given form. The properties of deposits, such as pH, red-ox potential, sorption capacity, type and amount of organic matter, content of carbonates and iron and manganese compounds affect the occurrence of metals as different species. The mobility of heavy metals accumulated in deposits and their toxicity to living organisms depends on the presence of those metals in potentially bioavailable forms whose quantitative and qualitative isolation is enabled by speciation analysis. Methods of sequential extraction provide important information on hazards to ecosystems from deposited heavy metals, which may become secondary sources of pollution as a result of chemical and biochemical processes, circulating within systems consisting of a bottom deposit, water, living organisms and a water course environment [6–12].

The aim of the study was to evaluate the content of zinc, copper and nickel and their amounts in isolated fractions of bottom sediments in the "Row Strzala" canal, channelling off post-treatment waters from the communal wastewater treatment plant in Siedlce to the Liwiec river, as well as in the river, upstream and downstream of the canal estuary.

Material and methods

The studied object comprised of bottom sediments from two water flows (the "Row Strzala" canal and Liwiec river) localized within the boundaries of Strzala and Chodow villages near Siedlce in eastern part of Mazovia region (Fig. 1). The "Row Strzala" is a canal that disposes reclaimed waters from municipal sewage treatment plant in Siedlce and storm sewage system to Liwiec river. Liwiec river is a right tributary of Bug river and one of the larger rivers on the South-Podlasie Lowland, that in its upper section flows through the Siedlce Upland. On studied area, these flows pass through agricultural areas (arable lands, meadows, pastures) built of sandy forms of water and glacial accumulation as well as shallow organic sediments (peats and organic silts) [13].

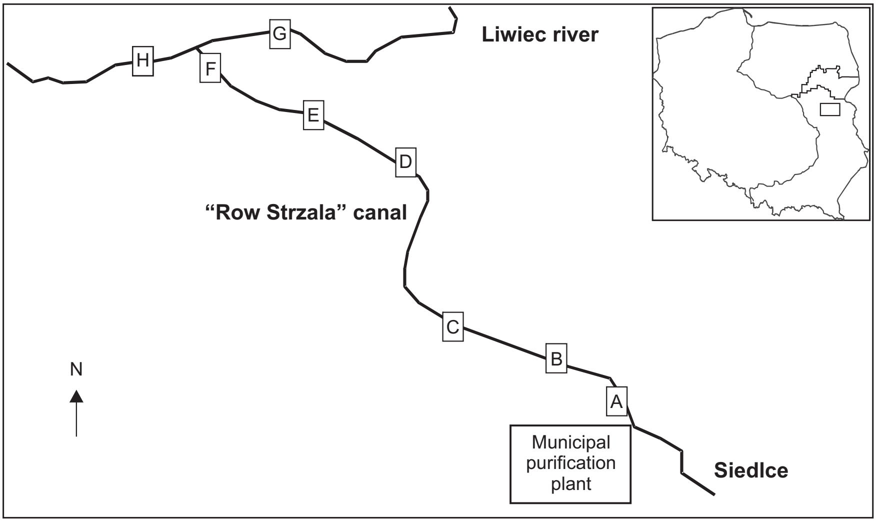

Fig. 1. The location of bottom sediments sampling sites in canal of the "Row Strzala" canal (A–F) and Liwiec river (G–H)

Samples were collected in polyethylene bags using a plastic scoop from surface layer of sediments (0–10 cm) at 8 representative points (three samples were taken from each point to obtain a representative sample on 10 m distance): 6 – in the "Row Strzala" bed (A, B, C, D, E, F), on distance of about 2 km between sewage treatment plant (N: $52^o11'37''$, E: $22^o15'24''$) and Liwiec river (N: $52^o12'33''$, E: $22^o13'56''$), and 2 – in Liwiec river bed, upstream – site G (N: $52^o12'37''$, E: $22^o11'14''$) and downstream – site H (N: $52^o12'30''$, E: $22^o13'42''$) of the canal estuary.

The bottom sediments samples air dried, sieved through a 2 mm mesh and then the following properties were determined: granulometric composition according to the Polish Soil Science Society [14] – by the *areometric* method, pH in 1 mol KCl $\cdot$ dm^{-3} – *potentiometrically*, the amount of organic carbon (C_{org}) – by the *oxidation-reduction* method [15]. *Cation exchange capacity* (CEC) values and the *index of soil saturation with base cations* (V) were calculated on the basis of *hydrolytic acidity* (HA) and the *sum of base exchangeable cations* determined by Kappen's method.

The total content of zinc (Zn_{tot}), copper (Cu_{tot}) and nickel (Ni_{tot}) were assessed by ICP-AES method (Optima 3200 RL, Perkin-Elmer) after homogenization bottom sediments samples in an agate mill and mineralization in mixture of concentrated HCl and HNO_3 (3:1) in a microwave system (Multiwave, Anton Paar).

The fractions of zinc, copper and nickel were determined by the *sequential extraction procedure* (in samples homogenized in an agate mill) proposed by The European Union's Standards, Measurements and Testing program (SM&T, formerly BCR) [7], in which four fractions were separated: F1 – *exchangeable*; F2 – *reducible*; F3 – *oxidizable*; F4 – *residual* (post-extractions remaining) (Table 1). The content of zinc, copper and nickel in particular fractions was determined by ICP-AES method. The percentage contribution of separated four fractions of Zn, Cu and Ni in relation to their total content were calculated. The suitability of the sequential extraction method was compared with that of the external standard method. The analysis also covered control samples, for which the identical analytical procedure was applied as for the study material. The analysis was conducted in triplicate and the tables show the average values.

Table 1

Reagents and reaction conditions of the sequential extraction procedure used in the investigated bottom sediments of the "Row Strzala" canal and Liwiec river

Fraction	Nominal target phase	Chemical reagents and conditions
F1 Exchangeable	Water and acid soluble species, cation exchange sites; specifically adsorbed ions and bound by weak electrostatic interactions	0.11 mol $CH_3COOH \cdot dm^{-3}$; pH = 3; shake for 16 h at 20 ^oC
F2 Reducible	Bound to iron and manganese oxyhydroxides	0.5 mol NH_2OH-HCl $\cdot dm^{-3}$; pH = 2; shake for 16 h at 20 ^oC
F3 Oxidizable	Bound to organic matter and sulfides	8.8 mol $H_2O_2 \cdot dm^{-3}$ (pH = 2–3); heat to 85 ^oC for 2 h (repeat again), and followed by 1 mol $CH_3COONH_4 \cdot dm^{-3}$ (pH = 2), and shake for 16 h at 20 ^oC
F4 Residual (post-extraction remaining)	Strongly associated to crystalline structures of minerals	Calculated as the difference between the total content of a particular heavy metals and the sum of their fraction: F1, F2, and F3, extracted during the previous steps

The relationships between Zn, Cu and Ni content in each fraction and selected properties of the bottom deposits under study were evaluated with linear correlation at two levels of significance $\alpha = 0.05$ and $\alpha = 0.01$.

Results and discussion

The bottom sediments under study were classified as weakly loamy sand and loose sand, whose selected physical, physicochemical and chemical properties are presented in Table 2. The pH values of the deposits was weakly acidic to alkaline (6.52–7.65) and their hydrolytic acidity (HA): 5.0–8.6 mmol(+) $\cdot$ kg^{-1}; the *sum of base exchangeable cations* (BEC): 49.0–272.0 mmol(+) $\cdot$ kg^{-1}, cation exchange capacity (CEC): 57.6––272.0 mmol(+) $\cdot$ kg^{-1}, the index of soil saturation with base cations (V): 85.1–98.1 % and *organic carbon content* (C_{org}): 0.68–19.6 g $\cdot$ kg^{-1}. The highest values of BEC, CEC and V and the lowest value of HA were found in samples with the highest organic carbon content (sites A, B and G). The pH values, the sum of base exchangeable cations, cation exchange capacity and the index of soil saturation with base cations as well as organic carbon and *clay fraction* ($\varnothing$ < 0.002 mm) content in deposits in the "Row Strzala" were found to decrease, while the value of hydrolytic acidity was found to increase with the distance from the wastewater treatment plant. Deposits in the Liwiec river were found to contain a higher content of C_{org} (8.59 g $\cdot$ kg^{-1}) and the values of BEC (141.3 mmol(+) · kg^{-1}), CEC (147.0 mmol(+) · kg^{-1}) and V (95.4 %) were also higher than those in the "Row Strzala" (7.13; 124.8; 132.0 and 91.8, respectively).

Table 2

The total content [mg · kg^{-1}] of Zn, Cu, Ni, and some properties of investigated bottom sediments of the "Row Strzala" canal (A–F), and Liwiec river (G–H)

Some properties	Sampling sites							
	A	B	C	D	E	F	G	H
Sand 2–0.5*	90	89	93	93	94	94	92	94
Silt 0.5–0.002*	7	7	4	5	4	4	6	3
Clay < 0.002*	3	4	3	2	2	2	2	3
Granulometric group	ps	ps	pl	pl	pl	pl	pl	pl
pH_{KCl}	6.86	7.22	6.85	6.64	6.63	6.52	7.65	6.88
HA [mmol(+) · kg^{-1}]	6.5	5.3	6.9	7.8	8.0	8.6	5.0	6.6
BEC [mmol(+) · kg^{-1}]	225.5	266.7	73.4	69.1	65.1	49.0	190.0	92.5
CEC [mmol(+) · kg^{-1}]	232.0	272.0	80.3	76.9	73.1	57.6	195.0	99.1
V [%]	97.2	98.1	91.4	89.9	89.1	85.1	97.4	93.3
C_{org} [g · kg^{-1}]	18.3	19.6	1.65	1.31	1.25	0.68	14.9	2.27
Zn_{tot} [mg · kg^{-1}]	115.3	124.1	36.0	55.1	57.4	72.1	27.1	65.4
Cu_{tot} [mg · kg^{-1}]	9.11	11.3	5.15	4.91	4.32	4.19	3.10	4.38
Ni_{tot} [mg · kg^{-1}]	5.22	6.08	4.02	3.49	3.30	3.18	2.26	3.38

* % fraction of diameter in mm; ps – weakly loamy sand, pl – loose sand; HA – hydrolitic acidity; BEC – the sum of base exchangeable cations; CEC – cation exchenge capacity; V – the index of soil saturation with base cations; Zn_{tot}, Cu_{tot}, Ni_{tot} – total content of Zn, Cu, Ni.

Licznar et al [4] and Skorbilowicz and Wiater [16] emphasised that the content of organic carbon and the granulometric composition of bottom deposits are affected by the soil in the drainage basin and they arise from transport and sedimentation of particles carried by water current. Accumulation of organic matter takes place in slowly flowing water and during periods of stagnation and affects the sorption properties of the deposits. High sorption capacity and saturation of the sorption complex with base cations have a beneficial effect on the buffer properties of bottom deposits which, in turn, affect sorption and desorption of heavy metals in an aquatic environment [4, 17].

The surface layer of the sediments (0–10 cm) was found to contain varied amounts of heavy metals whose decreasing average content [mg · kg^{-1}] is shown in the following order: Zn (69.1) > Cu (5.81) > Ni (3.95). The difference may be a result of the geochemical nature of an element and the properties of bottom deposits (pH, cation exchange capacity, organic carbon content and clay fraction – ∅ < 0.002 mm) [1]. The metal content was higher in the bottom deposits of the "Row Strzala" canal (average values: Zn – 76.7 mg · kg^{-1}, Cu – 6.50 mg · kg^{-1} and Ni – 4.33 mg · kg^{-1}) than in the Liwiec (46.3; 3.74 and 2.82 mg · kg^{-1}, respectively). The highest concentrations of the metals under study were found in the material taken from the canal near the wastewater plant (sites A and B) and the lowest were at a site situated upstream of its estuary to the

Liwiec (site G) (Zn – 27.1 mg · kg^{-1}; Cu – 3.10 mg · kg^{-1} and Ni – 2.26 mg · kg^{-1}). Higher concentrations of zinc (65.4 mg · kg^{-1}), copper (4.38 mg · kg^{-1}) and nickel (3.38 mg · kg^{-1}) in the bottom deposits of the Liwiec, taken at site H situated downstream of the canal estuary, resulted from their higher content in the deposits in the "Row Strzala" canal (Table 2).

The total content of zinc, copper and nickel at sites A and B and the content of zinc at sites D, E, F, H in the bottom deposits exceeded the values for the geochemical background for bottom sediments in Polish rivers (Zn 48.0 mg · kg^{-1}, Cu – 6.0 mg · kg^{-1}, Ni – 5.0 mg · kg^{-1}) [18]. According to the classification of water deposits proposed by Bojakowska [2], the deposits were included in class I – uncontaminated deposits, with the total content of Zn, Cu and Ni not exceeding the *lower potential toxicity threshold* (TEL) and not posing any threat to living organisms.

The highest content of heavy metals is found in bottom deposits near the source of contamination, but the elements can be transported downstream to lower sections of rivers with silt fractions and organic matter of deposits [1, 2, 19]. Skorbilowicz [3], Licznar et al [4], Skorbilowicz and Wiater [16, 20] and Ziola et al [21] examined bottom deposits in rivers and canals flowing through agricultural lands and found them to contain varied amounts of zinc (9.30–75.4 mg · kg^{-1}), copper (0.90–38.2 mg · kg^{-1}) and nickel (0.30–16.8 mg · kg^{-1}). Much more of those metals accumulate in bottom deposits in areas with high anthropopressure (industrial and communal sewage, mining industry, metallurgy, waste dumpsites) [9, 11, 19, 22–24]. Bottom sediments in Polish rivers, examined in the years 2003–2005 as part of the National Environment Monitoring programme, were found to contain varied amounts of Zn (7–12.000 mg · kg^{-1}), Cu (1–375 mg · kg^{-1}) and Ni (1–76 mg · kg^{-1}), with about 50 % of the deposits containing less than 125 mg · kg^{-1} of zinc and about 40 % of them containing less than 10 mg · kg^{-1} of copper and nickel [5].

The bottom deposits under analysis contained varied amounts of zinc, copper and nickel in four fractions, isolated sequentially by the BCR method (Table 3). The average percentage of the metals in the fractions is shown in the following sequences of decreasing percentage values of their total content: Zn – F2 (53.6) > F3 (21.0) > F4 (15.3) > F1 (10.2); Cu – F3 (50.4) > F4 (25.7) > F2 (15.0) > F1 (8.90); Ni – F4 (39.6) > F3 (26.6) > F2 (20.2) > F1 (13.6). Similar sequences for Zn, Cu and Ni fractions in deposits from different watercourses have been presented by Mossop and Davidson [8], Glosinska et al [9], Morillo et al [11], Purushothaman and Chakrapani [19], Karczewska et al [24], Stephens et al [25], Tuzen [26], Dabrowska [27], Sokolova et al [28], Rodrigues and Formoso [29].

The highest concentration of zinc in bottom deposits are usually found as combinations with Fe and Mn compounds (reducible fraction – F2), 20–75 % on average; copper is usually found in combinations with organic matter and sulphides (oxidizable fraction – F3), 30–59 % on average, while nickel forms stable combinations of the residual fraction (F4) – up to 90 % [1, 9, 11, 19, 22, 24–27, 29]. The average content of Zn, Cu and Ni in the most mobile and the most bioavailable exchangeable fraction (F1) in the bottom deposits under study (and, consequently, their capability of migrating to the water of the "Row Strzala" canal and the Liwiec) was the following: Ni (13.6 %) > Zn

(10.2 %) > Cu (8.90 %). A similar sequence in bottom deposits of the Kozlowa Gora water body was found by Dabrowska [27], while the proportion of Zn, Cu and Ni in mobile fractions of the Middle Odra river sediments was the following: Ni (12–59 %) > Cu (9–50 %) > Zn (7–36 %) [9].

Table 3

The percentage contribution of Zn, Cu, Ni fractions in the investigated bottom sediments of the "Row Strzala" canal (A–F) and Liwiec river (G–H)

Fractions	Sampling sites								Mean
	A	B	C	D	E	F	G	H	
Zn									
F1	5.28	5.64	10.9	11.3	12.7	13.0	8.74	13.7	10.2
F2	51.5	50.1	55.1	54.7	54.5	56.7	52.0	53.9	53.6
F3	32.5	32.0	18.1	17.6	16.2	13.4	23.5	14.7	21.0
F4	10.7	12.3	15.9	16.3	16.7	16.9	15.8	17.7	15.3
Cu									
F1	5.60	5.13	7.57	8.55	11.1	12.4	8.06	12.8	8.90
F2	9.11	10.3	12.6	16.9	20.1	22.0	13.5	15.5	15.0
F3	68.9	73.0	49.1	43.3	37.2	33.0	60.6	37.9	50.4
F4	16.4	11.6	30.7	31.2	31.6	32.6	17.7	33.8	25.7
Ni									
F1	13.2	10.5	13.0	14.5	15.7	15.9	10.3	15.6	13.6
F2	19.0	16.0	21.3	21.7	21.9	22.2	19.6	20.2	20.2
F3	29.9	34.5	27.1	24.1	22.4	21.5	30.7	22.5	26.6
F4	37.9	38.9	38.5	39.8	40.0	40.4	39.4	41.7	39.6

Fraction: F1 – exchangeable, F2 – reducible (bound to Fe-Mn oxide), F3 – oxidizable (bound to organic matter), F4 – residual.

The proportion of zinc, copper and nickel in the exchangeable (F1), reducible (F2) and residual (F4) fraction in the "Row Strzala" canal sediments increased with the distance from the wastewater treatment plant, reaching the maximum values before the estuary to the Liwiec, at site F. The percentage of the metals in the oxidizable fraction (F3) decreased with increasing distance from the wastewater treatment plant, reaching the minimum values at site F (Table 3). The bottom deposits taken in the Liwiec downstream of the canal estuary (site H), were found to contain higher proportion of Zn, Cu and Ni in fractions F1, F2 and F4 and their lower proportion in fraction F3 as compared with the site upstream of the canal estuary (G) (Table 3). The mobility of heavy metals contained in the exchangeable fraction (F1) increases at decreasing pH values and in variable red-ox conditions, especially in sandy formations, which poses a real and potential hazard to aquatic ecosystems and biotic links of the food chain [11, 19, 25]. When the pH is close to alkaline values, solubility and mobility of organic compounds of heavy metals increases, and their high percentage in fraction F1 in aquatic environment can be toxic to plants and animals [1, 6, 24]. Large amounts of metals in biologically inactive and stable mineral combinations of the residual fraction

(F4) and small amounts in the bioavailable and mobile exchangeable fraction (F1) are typical of uncontaminated deposits [11, 19, 22, 25, 26, 29].

Correlations between most of the examined parameters were found to exist in the bottom sediments under study (Table 4). Statistical analysis showed a significant negative effect of total content of zinc (Zn_{tot}), copper (Cu_{tot}) and nickel (Ni_{tot}), total organic carbon (C_{org}), cation exchange capacity (CEC) on the percentage of the metals in the exchangeable fraction (F1), with the strongest link existing for nickel (from $r = -0.753$ to $r = -0.830$). The content of the analysed metals in the reducible fraction (F2) correlated with the cation exchange capacity (Zn – $r = 0.936$; Cu – $r = 0.853$; Ni – $r = 0.927$; at $\alpha = 0.01$). A highly significant positive effect of the C_{org} content and CEC value on the amount of Zn, Cu and Ni in the oxidizable (F3) and residual (F4) fraction was observed, with the strongest relationships existing for copper ($r = 0.966$ and $r = 0.992$ for F3 and $r = 0.976$ and $r = 0.966$ for F4). Moreover, a significant relationship was observed in the analysed deposits between the amount of the clay fraction ($\varnothing < 0.002$ mm) and the percentage of zinc in fraction F4 ($r = 0.742$) and copper and nickel in fraction F2 ($r = 0.732$ and 0.806, respectively). The pH values of water deposits significantly correlated with the percentage of the metals in fraction F3 (Zn – $r = 0.831$; Cu – $r = 0.798$; Ni – $r = 0.776$).

Table 4

The correlation coefficients between the Zn, Cu, Ni fractions and some properties of the investigated bottom sediments

Zinc									
	F1	F2	F3	F4	Zn_{tot}	pH_{KCl}	C_{org}	CEC	$\varnothing < 0.002$
F1	x	–0.540	–0.832*	0.829*	–0.714*	–0.529	–0.742*	–0.781*	–0.563
F2		x	–0.767*	–0.654	0.776*	–0.382	0.308	0.936**	0.568
F3			x	–0.843**	0.458	0.831*	0.954**	0.937**	0.437
F4				x	0.621	–0.283	0.842**	0.936**	0.742*
Copper									
	F1	F2	F3	F4	Cu_{tot}	pH_{KCl}	C_{org}	CEC	$\varnothing < 0.002$
F1	x	0.819*	–0.825*	0.658	–0.733*	0.470	–0.780*	–0.806*	–0.544
F2		x	–0.826*	0.640	–0.651	–0.580	–0.688	0.853**	0.732*
F3			x	–0.957**	0.734*	0.798*	0.966**	0.992**	0.578
F4				x	0.647	–0.684	0.976**	0.966**	–0.448
Nickel									
	F1	F2	F3	F4	Ni_{tot}	pH_{KCl}	C_{org}	CEC	$\varnothing < 0.002$
F1	x	0.748*	–0.821*	0.260	–0.753*	–0.680	–0.809*	–0.830*	–0.437
F2		x	–0.807*	–0.118	0.255	–0.639	–0.683	0.927**	0.806*
F3			x	–0.856**	0.463	0.776*	0.913**	0.912**	0.578
F4				x	–0.069	–0.042	0.842**	0.876**	0.120

Significance at: $\alpha = 0.05$* ($r = 0.707$); $\alpha = 0.01$** ($r = 0.834$).
Fraction: F1 – exchangeable, F2 – reducible (bound to Fe-Mn oxide), F3 – oxidizable (bound to organic matter), F4 – residual.

Glosinska et al [9] examined bottom deposits and found a significant effect of the total content of zinc, copper and nickel on their content in fractions F1, F2, F3 i F4. Speciation of Zn, Cu and Ni in aquatic environment depends largely on the pH value and cation exchange capacity and organic carbon and clay fraction content [1, 11, 19, 25, 26].

Conclusions

1. Bottom sediments in the "Row Strzala" canal and in the Liwiec river downstream and upstream of the canal estuary were found to contain varied concentrations of zinc, copper and nickel and the content was higher in the canal deposits than the river deposits. The deposits under study were included in class I for metal content – uncontaminated deposits.
2. The average percentage of the analysed metals can be shown in the following sequence in decreasing order: for Zn F2 > F3 > F4 > F1; for Cu F3 > F4 > F2 > F1; for Ni F4 > F3 > F2 > F1.
3. The mobility of the metals in the deposits of the watercourses can be shown in the decreasing sequence of their content on the exchangeable fraction (F1): Ni > Zn > Cu.
4. As the distance from the wastewater treatment plant grew, the content of the metals under study in the exchangeable fraction (F1), reducible fraction (F2) and residual fraction (F4) of the bottom deposits of the "Row Strzala" canal increased and it decreased in the oxidizable fraction (F3).
5. The bottom deposits in the Liwiec, downstream of the canal estuary, were found to contain higher proportion of the metals under study in fractions F1, F2 and F4 and their lower content in fraction F3.
6. Statistical analysis has shown a significant effect of selected properties of the sediments (pH, C_{org}, CEC, clay fraction) on the speciation of zinc, copper and nickel.

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CYNK, MIEDŹ I NIKIEL W SEKWENCYJNIE WYDZIELONYCH FRAKCJACH Z OSADÓW DENNYCH

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Abstrakt: Badano zawartość ogólną cynku, miedzi i niklu oraz ich udział we frakcji wymiennej (F1), redukowalnej (F2), utlenialnej (F3) oraz rezydualnej (F4), wydzielonych według sekwencyjnej procedury rekomendowanej przez The European Union's Standards, Measurements, and Testing program (dawniej BCR), w osadach dennych kanału „Rów Strzała", odprowadzającego wody pościekowe z oczyszczalni ścieków komunalnych w Siedlcach i kanalizacji burzowej do rzeki Liwiec, a także w tej rzece, przed i za ujściem kanału, w miejscowościach Strzała i Chodów, na Wysoczyźnie Siedleckiej, we wschodniej części województwa mazowieckiego. W powierzchniowej warstwie (0–10 cm) badanych osadów stwierdzono zróżnicowaną zawartość metali ciężkich, których malejące średnie wartości (mg · kg^{-1}) przedstawiono w następującym szeregu: Zn (69,1) > Cu (5,81) > Ni (3,95). Zwartość ogólna Zn, Cu i Ni była większa w osadach dennych kanału niż rzeki. Najwięcej badanych metali stwierdzono w materiale pobranym z kanału w pobliżu oczyszczalni ścieków, a najmniej – w miejscu położonym powyżej jego ujścia do rzeki Liwiec. Osady badanych cieków zaliczono pod względem zawartości tych metali do klasy I – osadów nie zanieczyszczonych. Średni procentowy udział analizowanych metali w wydzielonych frakcjach, w stosunku do ich zawartości ogólnej, układał się w następujących szeregach malejących wartości dla Zn – F2 (53,6) > F3 (21,0) > F4 (15,3) > F1 (10,2); dla Cu – F3 (50,4) > F4 (25,7) > F2 (15,0) > F1 (8,90); dla Ni – F4 (39,6) > F3 (26,6) > F2 (20,2) > F1 (13,6). Mobilność metali w osadach badanych cieków wodnych układała się w szeregu ich malejącego średniego udziału we frakcji wymiennej (F1) następująco: Ni > Zn > Cu. Obliczenia statystyczne wykazały, że zawartość cynku, miedzi i niklu w wydzielonych frakcjach jest na ogół znacząco zależna między tymi metalami oraz wybranymi właściwościami badanych osadów dennych (pH, zawartość węgla związków organicznych, kationowa pojemność sorpcyjna, frakcja iłowa – ∅ < 0,002 mm).

Słowa kluczowe: osady denne, frakcje Zn, Cu, Ni, kanał Rów Strzała, rzeka Liwiec

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TRACE ELEMENT CONTENT IN CEREAL WEEDS AGAINST THE BACKGROUND OF THEIR SOIL CONTENTS
PART 3. CADMIUM AND NICKIEL CONTENTS IN SOIL AND WEEDS

ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W CHWASTACH ROŚLIN ZBOŻOWYCH NA TLE ICH ZAWARTOŚCI W GLEBIE
CZ. 3. ZAWARTOŚĆ KADMU ORAZ NIKLU W GLEBIE I CHWASTACH

Abstract: Thirty soil samples were collected from the 0–25 cm layer of arable land in the Brzeźnica commune in the first decade of June 2007. Samples of weeds commonly occurring in cereal crops, *ie* cornflower – *Centaurea cyanus* L., poppy – *Papaver rhoeas* L., corn chamomile – *Anthemis arvensis* and thistle – *Cirsium arvense* (L.) Scop. were collected from the same sites. In both soil and plant material were assessed total contents of cadmium and nickel and their soluble form contents.

Significant differences in cadmium and nickel contents, both approximate to total amount and soluble forms determined in 0.1 mol · dm^{-3} HCl solution were observed in the analyzed soils. The contents of soluble cadmium and nickel forms in soil were to the greatest extent dependent on the soil pH. It was revealed that in slightly acid and neutral soils the amount of extracted cadmium and nickel soluble forms was smaller in relation to the quantity of cadmium extracted from very acid soils with $pH_{KCl} < 5.5$.

Cadmium and nickel concentrations in the analyzed weeds from cereal crops ranged widely depending on their contents in soil and soil reaction, species and analyzed plant part. Cadmium content was diminishing with increasing pH_{KCl} value over 5.5, whereas the quantity of nickel accumulated in all analyzed weeds, both in their roots and aboveground parts was diminishing irregularly.

Keywords: weeds, soil, cadmium and nickel content, soil pH_{KCl}

The assessment of fodder or nutritive value of plants attaches great importance to their pollution with heavy metals. Weeds collected in cereal crops do not represent any fodder value, but their chemical composition may prove a valuable source of information about the level of the environment pollution with heavy metals. Under conditions of elevated levels of heavy metals in soil, one should seek the methods of

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their management which would allow limit their entering food chain. One of the most dangerous and toxic heavy metals is cadmium.

Heavy metal toxicity for living organisms is apparent when they are accumulated in the environment in excessive quantities [1–3]. Plants containing considerable amounts of heavy metals may constitute a serious source of these elements for humans and animals [1, 4]. Behaviour of heavy metals in soils and their phytoavailability depend on many factors: chemical, physical and biological processes, but also on soil properties [3, 5, 6].

The investigations were conducted to determine the contents of cadmium and nickel in selected weeds originating from cereal crops against these metals contents in soil.

Material and methods

Thirty soil samples were collected from the 0–25 cm layer of arable land in the first decade of June 2007 in order to assess their trace metal contents. The site where the soil samples and 30 samples of weeds most common in cereal crops: poppy – *Papaver rhoeas* L., cornflower – *Centaurea cyanus* L., corn chamomile – *Anthemis arvensis* L. and thistle – *Cirsium arvense* (L.) Scop. were collected was described in the previous part of the article in “Materials and methods” section [7].

Approximate to total contents of trace elements in the analyzed soils were determined following their mineralization at the temperature of 450 ^{o}C. Next they were digested in a mixture of perchloric(VII) and nitric(V) acids (2:3, v/v). Mineralized soil material was dissolved in hydrochloric acid (HCl) [8]. The contents of trace elements occurring in soluble compounds (soluble forms) were determined after extraction with 0.1 mol · dm^{-3} HCl solution, and the soil to extraction solution ratio was 1:10.

Collected plant material was washed, divided into the aerial parts and roots, dried, crushed and dry mineralized. The ash was dissolved in nitric(V) acid (1:2). In obtained solutions of the soil and plant samples, cadmium and nickel contents were assessed using ICP-AES method in JY 238 ULTRACE apparatus (Jobin Yvon Emission). Obtained results of these elements contents in soil and analyzed weeds were statistically elaborated.

Results and discussion

Characteristics of collected soil material

Considerable differences of the analyzed soils with reference to their granulometric composition, organic carbon content and pH were observed. The value of soil pH assessed in water suspension ranged from 4.81 to 7.68, whereas in 1 mol KCl · dm^{-3} solution from 3.95 to 6.64. Detailed data on physical and chemical properties of the analyzed soils were given in the previous paper [7]. The analyzed soil samples revealed considerable differences in cadmium and nickel total contents, as well as their soluble forms content.

Total cadmium content in the studied soils ranged from 0.48 to 3.52 mg · kg^{-1}, at geometric mean 1.12 mg Cd · kg^{-1}, whereas nickel contents ranged from 9.57 to 24.68 mg · kg^{-1}, at geometric mean 12.97 mg Ni · kg^{-1} (Table 1).

Table 1

Cadmium and nickel content in soil depending on soil reaction

Specification	Total content		Soluble form content	
	[mg · kg^{-1}]			
	Cd	Ni	Cd	Ni
pH in 1 mol KCl · dm^{-3} ≤ 5.5				
Arithmetic mean	1.35	14.67	0.79	1.93
Geometric mean	**1.22**	**14.14**	**0.78**	**1.78**
Range	0.68–3.52	10.38–24.68	0.46–0.98	0.71–5.03
Relative standard deviation [%]	53	30	16	56
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	1.16	12.01	0.71	1.64
Geometric mean	**1.05**	**11.72**	**0.68**	**1.44**
Range	0.48–1.45	9.57–10.03	0.38–1.09	0.81–1.43
Relative standard deviation [%]	50	26	29	57
pH in 1 mol KCl · dm^{-3} ≥ 6.6				
Arithmetic mean	0.88	11.16	0.67	1.02
Geometric mean	**0.87**	**11.15**	**0.66**	**1.01**
Range	0.81–0.95	10.47–11.86	0.63–0.69	0.91–1.08
Relative standard deviation [%]	8	6	4	4

The content of cadmium and nickel in soluble forms assessed in 0.1 mol · dm^{-3} HCl solution ranged from 0.38 to 1.09 mgCd · kg^{-1}, at geometric mean 0.73 mgCd · kg^{-1} and from 0.81 to 3.63 mgNi · kg^{-1}, at geometric mean 1.59 mgNi · kg^{-1} of soil. The amounts of the analyzed elements soluble forms to the greatest extend depended on the soil pH and organic carbon content (Table 2).

The amounts of soluble forms of cadmium and nickel extracted from slightly acid and neutral soils were smaller than the quantities of elements extracted from soil with pH_{KCl} below 5.5 (Table 1). For instance, the amount of nickel extracted with 0.1 mol · dm^{-3} HCl solution from slightly acid and neutral soils was by 19 and 43 % smaller in comparison with the quantity of nickel extracted from soils with pH_{KCl} below 5.5. The share of extracted soluble forms of cadmium and nickel in total content of these elements in soil fluctuated from 16 to 94 % for cadmium and from 7 to 27 % for nickel.

Karczewska [9] and Rogoz [10] demonstrated that a visible increase in metal salts solubility occurs when pH value decreases below 7.2 and therefore metals amount in soluble forms available to plants increases. Obtained results revealed that physical and chemical properties of the investigated soils differently affected total contents of cadmium and nickel and their soluble forms, as evidenced by simple correlation coefficients (Table 2).

Table 2

Simple correlation coefficients (r) between cadmium and nickel contents in soils and selected soil properties

Properties of soil	Total contents		Soluble forms	
	Cd	Ni	Cd	Ni
pH_{KCl} value	–0.351*	–0.413*	–0.375*	–0.344*
Content of C_{org}	0.272	0.352*	0.599***	0.429*
Share of fraction with diameter:				
< 0.02 mm	0.038	0.124	0.157	0.232
< 0.002 mm	0.155	0.359*	0.144	0.337

n = number of samples – 30; r significant at: *p = 0.05; **p = 0.01; ***p = 0.001.

On the basis of obtained results the analyzed soils were assessed considering degree of their pollution with cadmium and nickel on the basis of guidelines suggested by Kabata-Pendias et al [11]. Basing on these guidelines 14 samples were classified to soils with natural cadmium contents (0^o), 15 samples were classified to soils with elevated content of this element (I^o), whereas 1 sample represented a weakly polluted soil (II^o). In case of nickel, all analyzed soils were classified to the group with natural content of this element (0^o).

Contents of cadmium and nickel in the analyzed weeds

Contents of Cd and Ni in collected cereal weeds depended on: weed species, analyzed plant part and soil properties. Diversified trace element contents in plants depending on abiotic and biotic factors but also on individual variability of plants have been widely documented in the scientific literature [12–14].

Cadmium. Although no physiological role of cadmium has been determined so far, the element is exceptionally easily absorbed by plant, generally proportionately to its concentration in soil. This element contents in plants are greatly diversified, and the amounts most frequently assessed in the aboveground parts range from 0.05 to 0.2 mgCd · kg^{-1} [3].

Geometric mean content of cadmium in the analyzed roots of weed from cereal crops were arranged according to increasing content: poppy – 0.74 mgCd · kg^{-1}, thistle – 1.73 mgCd · kg^{-1}, cornflower – 2.20 mgCd · kg^{-1} and chamomile – 3.30 mgCd · kg^{-1}, whereas in the aerial parts of the weeds geometric mean cadmium content was arranged as follows: poppy – 0.34 mgCd · kg^{-1}, cornflower – 1.37 mgCd · kg^{-1}, thistle – 1.94 mgCd · kg^{-1} and chamomile – 2.60 mgCd · kg^{-1} (Table 3).

Table 3

Cadmium and nickel content in cereal weeds depending on soil reaction

Mean content	Roots		Aboveground parts	
	Cd	Ni	Cd	Ni
Cornflower – *Centaurea cyanus* L.; n = 30				
pH in 1 mol KCl · dm^{-3} ≤ 5.5				
Arithmetic mean	3.67	4.48	2.06	2.44
Geometric mean	**3.29**	**3.92**	**1.94**	**2.17**
Range	1.45–7.32	1.11–10.06	0.99–3.58	1.11–6.24
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	1.36	2.63	0.95	1.71
Geometric mean	**1.18**	**2.42**	**0.90**	**1.41**
Range	0.43–1.65	1.37–5.09	0.35–1.28	0.65–3.62
pH in 1 mol KCl · dm^{-3} ≥ 6.5				
Arithmetic mean	2.01	3.16	1.15	1.91
Geometric mean	**1.84**	**3.09**	**1.08**	**1.83**
Range	1.17–3.23	2.29–3.72	0.74–1.73	1.33–2.65
Poppy – *Papaver rhoeas* L.; n = 30				
pH in 1 mol KCl · dm^{-3} ≤ 5.5				
Arithmetic mean	1.48	2.47	0.83	1.98
Geometric mean	**1.06**	**2.20**	**0.46**	**1.65**
Range	0.13–6.45	1.14–5.62	0.11–5.18	0.66–4.61
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	0.47	1.47	0.25	1.29
Geometric mean	**0.44**	**1.30**	**0.22**	**1.12**
Range	0.24–0.83	0.82–3.80	0.13–0.57	0.85–3.80
pH in 1 mol KCl · dm^{-3} ≥ 6.5				
Arithmetic mean	0.54	1.82	0.28	1.52
Geometric mean	**0.49**	**1.70**	**0.24**	**1.38**
Range	0.33–0.85	1.18–2.81	0.12–0.52	0.91–2.49
Corn chamomile – *Anthemis arvensis* L.; n = 30				
pH in 1 mol KCl · dm^{-3} ≤ 5.5				
Arithmetic mean	6.21	5.06	4.50	2.78
Geometric mean	**4.98**	**4.31**	**3.63**	**2.26**
Range	1.82–13.93	1.32–9.28	1.17–10.02	0.73–7.40
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	2.71	2.44	2.24	1.70
Geometric mean	**1.99**	**2.18**	**1.55**	**1.46**
Range	0.21–7.58	1.11–4.88	0.82–10.12	0.56–3.52

Table 3 contd.

Mean content	Roots		Aboveground parts	
	Cd	Ni	Cd	Ni
pH in 1 mol KCl · dm^{-3} ≥ 6.5				
Arithmetic mean	1.83	2.24	1.93	1.64
Geometric mean	**1.71**	**2.05**	**1.89**	**1.61**
Range	1.02–2.49	1.11–3.10	1.46–2.37	1.35–2.15
Thistle – *Cirsium arvense* (L.) Scop.; n = 30				
pH in 1 mol KCl · dm^{-3} ≤ 5.5				
Arithmetic mean	2.79	3.76	4.28	3.77
Geometric mean	**2.47**	**3.25**	**3.41**	**3.02**
Range	1.01–5.42	1.41–8.98	1.05–17.35	1.05–8.69
pH in 1 mol KCl · dm^{-3} from 5.5 to 6.5				
Arithmetic mean	1.36	2.05	1.09	2.98
Geometric mean	**1.17**	**1.93**	**1.01**	**2.61**
Range	0.64–3.69	1.01–3.62	0.52–1.54	1.33–5.98
pH in 1 mol KCl · dm^{-3} ≥ 6.5				
Arithmetic mean	0.91	2.07	1.29	1.77
Geometric mean	**0.81**	**1.79**	**1.09**	**1.62**
Range	0.39–1.27	0.79–3.09	0.55–2.29	0.92–2.59

Nickel. Nickel is an element relatively easily absorbed by plants. If it occurs in soils in its mobile forms, it is taken up proportionately to its content in soil.

Nickel content in the studied weeds was quite diversified depending on the species, analyzed plant part and soil pH. Geometric mean nickel content in the roots of the analyzed cereal weeds can be arranged according to its growing contents: poppy – 1.83 mgNi · kg^{-1}, thistle – 2.51 mgNi · kg^{-1}, corn chamomile – 3.19 mgNi · kg^{-1} and cornflower – 3.25 mgNi · kg^{-1},whereas the aboveground parts of these weeds were ordered as follows: poppy – 1.44 mgNi · kg^{-1}, cornflower – 1.78 mgNi · kg^{-1}, corn chamomile – 1.89 mgNi · kg^{-1} and thistle – 2.57 mgNi · kg^{-1} (Table 3).

Irrespectively of changes of pH values in the studied soils, higher values of cadmium and nickel were assessed in roots than in the aboveground parts of the analyzed weeds. It evidences poor translocation of these metals from roots to the aboveground parts (Table 3). In their investigations Jurkowska et al [12] revealed considerable interspecies differences in transport of these trace elements from the roots to the aboveground parts in plant species belonging to the same family (legumes).

Cadmium content in roots and aboveground parts of the analyzed weeds of cereal crops was decreasing when the pH_{KCl} value of the analyzed soils was increasing above 5.5. For instance, geometric mean cadmium content in corn chamomile from slightly acid and neutral soils was smaller, respectively by 40 % and 66 % as compared with geometric mean cadmium content in corm chamomile roots from soils with pH_{KCl}

below 5.5 (Table 3). Increase in pH_{KCl} value above 5.5 in the studied soils not unanimously affected nickel contents in the analyzed weeds. Assuming e.g. geometric mean nickel content in the roots and aboveground parts of cornflower grown on soils with $pH_{KCl} \leq 5.5$ as 100, we will see that this element content in the roots of cornflower from slightly acid and neutral soils was smaller by 35 % and 16 % (Table 3).

Statistical analysis of the obtained results revealed that some physicochemical properties of the researched soils not unanimously affected the contents of the analyzed elements in weeds from cereal crops (Table 4). A significantly negative dependence was revealed between the soil pH and cadmium content in cornflower roots, where $r = -0.616$; $p = 0.001$ and in the aboveground parts $r = -0.672$; $p = 0.001$ (Table 4).

Table 4

Values of simple correlation coefficients (r) between selected soil properties and cadmium and nickel contents in cereal weeds

Properties of soil; n = 30	Roots		Aboveground parts	
	Cd	Ni	Cd	Ni
Cornflower – ***Centaurea Cyanus* L.**; n = 30				
pH_{KCl} value	–0.616***	–0.440*	–0.672***	–0.297
Total content	0.473**	0.452**	0.389*	0.670***
Soluble forms	0.253	0.549**	0.342*	0.635**
Poppy – ***Papaver rhoeas* L.**; n = 30				
pH_{KCl} value	–0.473**	–0.327	–0.336*	–0.268
Total content	—	—	—	—
Soluble forms	—	0.343	—	—
Corn chamomile – ***Anthemis arvensis* L.**; n = 30				
pH_{KCl} value	–0.568**	–0.545**	–0.544**	–0.449**
Total content	0.594**	0.422*	0.548**	0.591***
Soluble forms	0.416*	0.447**	0.291	0.518**
Thistle – ***Cirsium arvense* (L.) Scop.**; n = 30				
pH_{KCl} value	–0.636***	–0.541**	–0.458**	–0.314
Total content	0.054	0.086	0.057	0.182
Soluble forms	0.370*	0.006	0.207	0.167

n = number of plant samples; r significant at: *p = 0.05; **p = 0.01; ***p = 0.001.

On the basis of obtained results the contents of cadmium and nickel were assessed in the analyzed plants assuming the guidelines suggested by Kabata-Pendias et al [11] for plants designed for human consumption and animal fodder. Basing on these guidelines exceeded values of critical cadmium content, *ie* 0.5 $mgCd \cdot kg^{-1}$ were assessed in 70 % of weed samples, whereas no cases of exceeded nickel content were assessed in the studied weeds. High level of cadmium contents in the investigated weeds from cereal crops may suggest that this element contents may have been exceeded also in cereals.

Conclusions

1. Total contents of cadmium and nickel and their soluble forms were diversified in the analyzed soils. With increasing soil pH_{KCl} over 5.5 total contents of these elements and their soluble forms decreased.

2. The contents of cadmium and nickel in the analyzed weeds present in cereal crops ranged widely depending on the species, analyzed plant part, these elements total content in soil and their soluble forms contents, as well as soil reaction.

3. With increasing soil pH_{KCl} over 5.5 the contents of cadmium and nickel decreases in all analyzed weeds, both in their roots and the aboveground parts.

4. The studied plants revealed elevated cadmium contents. In 70 % of weed samples Cd content exceeded permissible value of this element, *ie* over 0.5 mgCd $\cdot$ kg^{-1} dry mass was assessed.

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ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W CHWASTACH ROŚLIN ZBOŻOWYCH NA TLE ICH ZAWARTOŚCI W GLEBIE

CZ. 3. ZAWARTOŚĆ KADMU ORAZ NIKLU W GLEBIE I CHWASTACH

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Abstrakt: W pierwszej dekadzie czerwca 2007 r. na terenie gminy Brzeźnica pobrano 30 próbek glebowych z gruntów ornych z warstwy 0–20 cm. Z tych samych miejsc pobrano próbki chwastów powszechnie występujących w uprawach roślin zbożowych, tj.: chaber bławatek – *Centaurea cyanus* L., mak polny – *Papaver rhoeas* L., rumian polny – *Anthemis arvensis* L. oraz ostrożeń polny – *Cirsium arvense* (L.) Scop. W zebranym materiale glebowym oznaczano całkowite zawartości kadmu i niklu oraz ich zawartości w formach rozpuszczalnych. W materiale roślinnym oznaczano zawartości kadmu i niklu.

Zaobserwowano istotne różnice zbliżonej do całkowitej zawartości kadmu i niklu w badanych glebach, jak również ich w form rozpuszczalnych oznaczonych po ekstrakcji roztworem HCl o stężeniu 0,1 mol $\cdot$ dm^{-3}.

Zawartość rozpuszczalnych form kadmu i niklu w glebach w największym stopniu zależały od ich odczynu. Wykazano, że w glebach lekko kwaśnych i obojętnych ilość wyekstrahowanych rozpuszczalnych form kadmu i niklu była mniejsza w odniesieniu do ich ilości wyekstrahowanych z gleb bardzo kwaśnych $pH_{KCl} < 5,5$.

Zawartości kadmu oraz niklu w badanych chwastach rosnących w uprawach roślin zbożowych wahały się w szerokim zakresie w zależności od ich zawartości w glebie i odczynu oraz od gatunku i analizowanej części rośliny. Wraz ze wyrostem wartości pH_{KCl} powyżej 5,5 zmniejsza się zawartość kadmu, natomiast ilość akumulowanego niklu we wszystkich analizowanych chwastach, tak w korzeniach, jak i w częściach nadziemnych, zmniejszała się nieregularnie.

Słowa kluczowe: chwasty, gleba, zawartość kadmu i niklu, pH_{KCl} gleby

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CHANGES OF FERTILIZER COMPONENTS AND HEAVY METAL CONTENTS DURING COMPOSTING PROCESS

ZMIANY ZAWARTOŚCI SKŁADNIKÓW NAWOZOWYCH ORAZ METALI CIĘŻKICH W TRAKCIE PROCESU KOMPOSTOWANIA

Abstract: The changes of fertilizer components and heavy metal contents were analyzed in selected municipal wastes during composting process while the quality of produced compost was assessed in view of its impact on the environment. The material for analyses was provided by a mixture of selected wastes from green areas subjected to composting process using MUT-Kyberferm technology. Contents of organic carbon, potassium, phosphorus, heavy metals and total nitrogen were assessed in the collected samples.

Contents of organic carbon diminished with composing time, opposite to changes of nitrogen content, which were increasing. Composting proceeded showing a considerable dynamics of organic carbon content changes. Heavy metal contents did not exceed the values permissible for organic fertilizers. Results of organic carbon and heavy metal contents analysis in the tested compost indicate its potential application in agriculture, which is a rational way of organic waste material management.

Keywords: compost, fertilizer components, heavy metals

Municipal wastes pose an increasingly serious problem for developing city agglomerations. Their storage usually involves setting aside large areas of agricultural land, degradation of the environment due to water, soil and atmosphere pollution with chemical or microbiological factors [1]. Selective collection of green wastes led to development of various composting technologies and in consequence to setting up separate objects in which this process is carried on [2].

Organic recycling of wastes, including composting, should be treated as an important method of their recovery. In result of the intensification of changes which occur during composting the wastes may be fully disposed of a commercial product, *eg* organic fertilizer may be obtained. Processes occurring during composting favour the matter

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transformation whereas nutrients became better available to plants in compost than in the initial material.

The aim of the paper was an analysis of changes of fertilizer components and heavy metal contents occurring during composting process conducted on a technological scale on organic material obtained from green areas in Krakow. The results will be compared with the results obtained in the analysis of the process conducted in a laboratory scale.

Material and methods

Initial material was prepared in a composting plant of green wastes in Krakow--Płaszow; it was a mixture of selected fractions of wastes, mainly from green areas, subjected to composting process. The following wastes were used for initial material preparation: grass 29.89 %; fine cuttings 26.77 %, fresh cuttings 23.2 %; leaves 9.06 %; cereal wastes 6.91 % and kitchen wastes 4.11 %. The cereal wastes consisted of cereal chaff originating from cereal processing plant in Krakow, whereas kitchen wastes came from restaurants and canteens in Krakow. Each time the samples of materials for analysis were collected from one, determined windrow, in pursuance of branch standard PN-R-04006:2000 at monthly intervals during the period from October 2008 to March 2009. Five individual samplings from various windrow sites constituted a collective sample. A sample collected in October was the initial material after leaving the reactor chamber, *ie* after completing the phase of intensive composting. The following samples were taken from ripening material. Initially it was ripening compost in intermediate ripening hall (sample collected in November), subsequently compost which was ripening on the composting plant yard.

The composting was carried out using MUT-Kyberferm technology, which is a chamber composting technology. The first – thermophilous phase comprises intensive composting in a reactor for 14 days. The bioreactor is a closed installation of concrete placed in a hall. The wastes in the bioreactors are vacuum aerated through a system of pipes with a condensate trap. Fresh air supplied to the bioreactors is heated and watered. Condensate, or the effluents are used for material moistening, which allows to use the installation without using tap water. The second phase is intermediate ripening in the composting plant hall for 3 weeks, whereas the third phase involves final ripening for three weeks in windrows on the square.

Collected material was subjected to chemical analysis which determined dry mass content in samples with natural moisture after their drying at the temperature of 70 ^{o}C in a dryer with hot air flow. Laboratory analyses were conducted in two replications.

The following assessments were conducted in dried and crushed compost samples:

– total nitrogen by means of Kjeldahl method, after sample mineralization in concentrated sulphuric(VI) acid,

– potassium, phosphorus, calcium, sodium and heavy metals using ICP-AES method after sample mineralization in a muffle furnace (450 ^{o}C for 5 hours) and dissolving the remains in nitric(V) and chloric(VII) (perchloric) acids,

– organic carbon in a mixture of potassium dichromate(VI) and concentrated sulphuric(VI) acid using oxidative-titrating method,

– organic matter as losses after sample mineralization in a muffle furnace (450 ^{o}C for 5 hours),

– pH by potentiometer in a suspension of organic material and water, maintaining dry matter to water ratio 1:10,

– electrolytic conductivity – by conductometer.

Mean values for analytical replications for each date presented in Tables were interpreted in the paper. Statistical analysis was conducted using Statistica 9 programme.

Results

Analysis of collected material chemical composition revealed (Table 1) a diversification of dry mass content (33.8–47.6 %), due to the character of the technological process. Compost was ripening in windrows on the composting plant yard, irrespective of weather conditions, from November to March. Snowfall and rainfall might have caused its periodical excessive moistening.

Table 1

Selected properties of compost during composting process

Month of composting	Dry matter [%]	Electrolytic conductivity [mS · cm^{-1}]	pH	Organic matter	C_{tot}	N_{tot}	C:N
				[g · kg^{-1} d.m.]			
October	47.5 ± 1.56	6.3 ± 0.35	6.3	697 ± 0.71	294.2 ± 2.34	16.4 ± 0.08	18
November	36.0 ± 0.85	4.16 ± 0.19	7.0	579 ± 8.99	253.5 ± 5.80	18.5 ± 0.02	14
December	51.9 ± 2.83	3.88 ± 0.09	7.2	557 ± 15.53	208.6 ± 8.08	16.6 ± 0.09	13
January	42.1 ± 1.06	2.93 ± 0.12	7.2	547 ± 0.82	203.7 ± 17.66	19.2 ± 0.01	11
February	38.6 ± 0.64	3.75 ± 0.04	7.5	511 ± 18.80	207.0 ± 5.62	16.1 ± 0.12	13
March	41.1 ± 0.14	2.82 ± 0.04	7.7	522 ± 13.08	198.5 ± 3.16	19.0 ± 0.04	10

± SD (standard deviation), n = 2.

The reaction of the initial material on pH scale was 6.3 (Table 1). After a month of composting the analyzed materials revealed a neutral reaction, which was growing with the time of the process duration. Value of electrolytic conductivity in the final product was 3.82 mS · cm^{-1} and decreased by half in comparison with the initial material (6.30 mS · cm^{-1}) (Table 1).

Content of organic matter was decreasing with duration of composting time and ranged from 697 g · kg^{-1} d.m. in October to 522 g · kg^{-1} d.m. in March. Parallel with losses of organic matter, total carbon content was also diminishing (Table 1).

Total nitrogen content showed an opposite relationship. It fluctuated on the level from 16.4 gN · kg^{-1} d.m. in the material taken out from the bioreactor chamber to 19.2 gN · kg^{-1} d.m. in the subsequent phases of composting. The amount of ash in the composted mass was also increasing (Table 1).

Because of the total carbon to total nitrogen ratio, compost may be regarded as stabile at each phase of the process after intensive composting. C:N ratio was decreasing with composting time reaching 18 in the compost leaving bioreactor chamber and 10 in the final product (Table 1).

The contents of phosphorus, potassium and sodium in the compost revealed slight diversification. Increase in calcium content occurred mainly after the first month of composting. Content of each of the macroelements in the final product increased in comparison with the initial material (Table 2).

Table 2

Fertilized components content during composting process

Months of composting	P	K	Ca	Na
	$[g \cdot kg^{-1}$ d.m.]			
October	2.2 ± 0.27	6.8 ± 3.36	20.7 ± 0.85	0.7 ± 0.05
November	2.5 ± 0.22	9.8 ± 0.80	26.8 ± 0.08	0.9 ± 0.03
December	2.7 ± 0.30	10.0 ± 0.17	29.3 ± 0.20	1.0 ± 0.01
January	3.1 ± 0.34	10.1 ± 0.67	30.7 ± 1.02	1.0 ± 0.01
February	2.7 ± 0.17	9.8 ± 0.94	30.7 ± 0.20	1.1 ± 0.01
March	2.7 ± 0.49	8.4 ± 0.38	30.7 ± 0.16	1.0 ± 0.01

± SD (standard deviation), n = 2.

An important criterion of compost assessment in view of its environmental application (mainly in agriculture) is determining its heavy metal contents. Analysis of the total contents of selected metals (Cd, Cu, Zn) (Table 3) allowed to classify the final product – ripe compost to I quality class (according to limits suggested by the European Commission) [4].

Table 3

Trace elements content during composting process

Months of composting	Cd	Cu	Zn
	$[mg \cdot kg^{-1}$ d.m.]		
October	0.41 ± 0.06	19.2 ± 2.64	112.3 ± 13.62
November	0.56 ± 0.01	26.0 ± 1.65	127.8 ± 5.93
December	0.62 ± 0.12	20.4 ± 1.54	141.4 ± 7.25
January	0.90 ± 0.07	33.9 ± 0.04	210.5 ± 9.64
February	0.71 ± 0.02	36.9 ± 4.23	162.4 ± 4.51
March	0.68 ± 0.04	48.2 ± 1.55	212.8 ± 2.31

± SD (standard deviation), n = 2.

Compost sampled in October contained 0.41 mgCd · kg^{-1} d.m., in January the content increased to 0.90 mgCd · kg^{-1} d.m. and subsequently it stabilized on the level of

0.68 mg · kg^{-1} d.m. in March. Differences in cadmium concentrations were statistically non-significant (Table 3).

Copper and zinc contents were increasing with the composting time. The amount of copper grew from the level of 19.2 to 48.2 mgCu · kg^{-1} d.m., while zinc amount at the beginning of the process was 112.3 mgZn · kg^{-1} d.m. and increased to 212.8 mgZn · kg^{-1} d.m. in the ripe product (Table 3).

Homogenization of material and its stabilization were progressing with the time of composting. It has been indicated by diminishing values of standard deviation in a majority of analyzed parameters (Tables 1–3).

Discussion

Application of some waste materials for fertilization purposes is difficult or sometimes impossible because of their contents of excessive amounts of harmful elements. The elements which most seriously limit the use of some waste materials are heavy metals and pathogenic organisms. Another limitation may be poor physical parameters of the materials. Therefore, a technology is sought which could improve physical, chemical and sanitary properties of such wastes and in result upgrade them [5]. Priorities of waste management policy make composting one of the most common methods of utilisation of dispensable organic mass. Baran et al [1, 7] think that composts of some fractions of selected wastes and mixed wastes is a fertilizer generally characterized by a high contents of nitrogen, phosphorus and potassium, whereas the contents of heavy metals usually do not exceed limit values.

On the basis of chemical analysis conducted on the tested compost it may be stated that mineralization of organic matter was particularly apparent during the thermophilous phase, as evidenced by decreasing content of total carbon content and considerable increase in ashes amount in the composted biomass. The content of organic compounds was diminishing along with various changes intensity during composting [3, 6].

Nitrogen transformations were occurring parallel with organic matter transformation process. Various intensity of ammonification, nitrification and denitrification processes at individual composting phases shaped the total N content. The amount of total N was growing in the ripening compost, which has been confirmed also in papers by other authors [2, 3].

At the final phases of composting a stabilization of organic matter mineralization occurred and the degree of its humification was increasing, which favoured stabilization of C:N ratio. The index assumes the value of 10 at the final phase of composting, which may evidence a high value of produced compost. The fact has been corroborated among others by Siuta [8], Jedrczak [2] and Jimenez and Garcia [9]. Value of electrolytic conductivity was decreasing, which testifies a decreased salinity and improves fertilizer value of the compost [2].

The ripening processes occurring in the discussed compost affected the total content of macroelements. Compost revealed macroelement contents on the level reported by a majority of authors [1, 5, 7, 10, 11].

Potassium content in the analyzed compost increased slightly during composting process and considering the results obtained by Gondek [5] it may evidence this element deficiency in composts. Also Kalembasa et al [12] indicate considerable deficiencies of potassium in the compost manufactured using "GWDA" technology. A decrease in potassium content may be caused by its losses with water leaching from the windrow. Changes in this element content confirm a tendency for changes in electrolytic conductivity. Phosphorus content changed slightly during composting process. Eventually, it assumed the value of 3.16 gP $\cdot$ kg^{-1} d.m., approximate for most composts [10]. Densification of the content which in this case occurred was caused by carbon losses.

Also heavy metal contents were densified. Unlike the organic components of compost, heavy metals do not undergo biological breakdown, therefore ripe material becomes enriched in metals in comparison with the fresh material [13].

Compost manufactured from mixed municipal wastes often contains relatively high amounts of lead, cadmium, copper and zinc. Because most of these elements is present also in some waste materials, they become unsuitable for composting [2]. The guidelines limiting heavy metal contents aim at differentiation of products suitable for use from those unsuitable as raw materials for composting [13]. In the presented investigations the composted material consisted of selectively gathered wastes from green areas. Obtained compost was characterized with heavy metal contents not exceeding the permissible limits, which indicates suitability of these wastes for composting and lack of pollution in the areas where they were acquired.

Conclusions

1. Composting time significantly affected improvement of some parameters evidencing the ripeness and quality of compost.
2. Changes of fertilizer components and heavy metal contents occurred mainly after completion of the first composting phase.
3. Composting of selected fractions of wastes, mainly from green areas in Krakow, allows to obtain a product abundant in organic substance and basic biogens with considerable fertilizer value and indicates potential use of the compost in agriculture.
4. Heavy metal contents were much lower than the amounts permissible by regulations suggested by the EU and allowed to classify the compost to I class.

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ZMIANY ZAWARTOŚCI SKŁADNIKÓW NAWOZOWYCH ORAZ METALI CIĘŻKICH W TRAKCIE PROCESU KOMPOSTOWANIA

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Abstrakt: Podjęto badania, których celem było określenie zmian zawartości składników nawozowych oraz metali ciężkich, zachodzących w czasie kompostowania wybranych odpadów komunalnych. Materiał do badań stanowiła mieszanina wyselekcjonowanych odpadów z utrzymania terenów zielonych, poddana procesowi kompostowania według technologii MUT-Kyberferm. Próbki pobrano w odstępach miesięcznych z kompostowni w Krakowie-Płaszowie. W pobranych próbkach materiałów organicznych oznaczono zawartość węgla organicznego, zawartość potasu i fosforu, metali ciężkich oraz azot ogólny.

Zawartość węgla organicznego zmniejszała się wraz z upływem czasu kompostowania, przeciwnie do zmian zawartości azotu, która zwiększała się. Kompostowanie przebiegało z dość dużą dynamiką zmian zawartości węgla organicznego. Zawartości metali ciężkich nie przekroczyły wartości dopuszczalnych dla nawozów organicznych. Wyniki badań zawartości węgla organicznego, pozostałych składników nawozowych i metali ciężkich w badanym kompoście wskazują na możliwość wykorzystania tych wyników w rolnictwie. Jest to racjonalny sposób zagospodarowania odpadowych materiałów organicznych.

Słowa kluczowe: kompost, składniki nawozowe, metale ciężkie

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GEOSTATISTICAL ANALYSIS OF SPATIO-TEMPORAL VARIABILITY OF SOIL MICROBIAL BIOMASS AND ITS ACTIVITY AT A PLOT SCALE

ANALIZA GEOSTATYSTYCZNA ZMIENNOŚCI CZASOWO-PRZESTRZENNEJ GLEBOWEJ BIOMASY MIKROBIOLOGICZNEJ I JEJ AKTYWNOŚCI W SKALI POLETKOWEJ

Abstract: Analysis and interpretation of spatio-temporal variability of soil microbial biomass content (*microbial biomass carbon* – MBC and nitrogen – MBN) and activity (dehydrogenase – DH, and fluorescein diacetate hydrolysis – FDAH, soil basal respiration – BR_3) and their relationship to the variability of some physicochemical properties at the surface horizon of Phaeozem were studied. Soil samples were collected at 50 points at regular intervals 10 × 10 m in April and August 2007. Both biomass C and N concentration and FDAH activity showed significantly higher values in April than in August, while DH activity and BR_3 range did not significantly differ between both sampling months. To characterise the spatial variability of the properties, spherical, linear or mixed (spherical/linear) models with ($BR_{3,}$ FDAH and MBC in April) or without (DH, FDAH, MBN and MBC in August) the nugget effect, were fitted to the calculated semivariograms. Soil basal respiration and FDA hydrolysis activity (April) were in moderate variability class (the nugget effect between 25 and 75 %), while only MBC in April was in the weak variability class (the nugget effect < 25 %). The ranges of influence calculated for microbiological properties data ranged from 10 to 17 m. Kriged maps displayed irregular distribution of microbial properties in the soil surface and their spatial distribution varied between April and August.

Keywords: spatio-temporal variability, geostatistics, soil microbial biomass, FDA hydrolysis, dehydrogenase, soil respiration

Soil properties are inherently variable in nature mainly due to geologic and podologic soil forming factors (*eg* parent material, vegetation, climate), but heterogeneity can be

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also induced by agricultural managements, like tillage, fertilization, crop rotation [1]. Soil spatial variability can occur in different spatial scales, ranging from microscale (millimeters, centimeters) and plot level (meters), up to the landscape scale (kilometers) [2]. Knowledge of spatial variability is important in natural resource management, interpolation and soil sampling design [3]. Most studies of soil spatial structure focus on abiotic soil properties such as moisture, pH, hydraulic conductivity, CEC, and texture [1, 4]. Fewer studies are focused however on properties related to soil microbial activity. Microbial biomass and activity are critical to soil ecosystem function and are sensitive indicators of ecosystem perturbations [5]. They may therefore to exhibit high spatial variability even in uniformly managed field. Moreover, within the same area spatial structure may change significantly with time [6].

The main application of geostatistical techniques in soil science is the detection, estimation and mapping of soil properties in unsampled areas [7]. Geostatistics comprises two components (a) modeling the spatial variation to create the semivariogram, and (b) kriging to produce maps [8]. Semivariograms describe the semivariance (a measure of property variance) between sampling locations at a different lag distance [9]. Kriging is a linear interpolation procedure that provides estimates at unsampled sites [10]. Kriging estimates are calculated as weighted sums of the adjacent sampled concentrations. That is, if data appear to be highly continuous in space, the points closer to those estimated receive higher weights than those farther away [11]. The last step involved in the geostatistical approach includes the display of spatial pattern using contour (kriged) maps (10].

The objective of the study was to determine the spatio-temporal structure of microbial biomass and activity and related soil chemical properties at a plot scale.

Material and methods

Soil samples were collected from an agricultural field located at the Orlinek village, near Mrocza in the Pomerania and Cuiavia region, northwest Poland. The area that was selected for the research is partially covered with Phaeozem [12]. At the year of sampling (2007) the field was planted with winter wheat (*Triticum aestivum* L.) with the spring rape as a forecrop. Soil samples were taken twice a year from the surface area of soil profile: at the stage of the winter wheat spreading (on 12 April 2007) and directly after harvest. The basic sampling design was a rectangle 40 × 90 m and samples were collected at regular intervals 10 × 10 m, resulting in 50 samples in each sampling date. Each sample was mean of 10 subsamples taken randomly from a circular area with a radius of 2 m from the node point.

Dehydrogenase activity was tested by reduction of 2, 3, 5-triphenyltetrazolium chloride (TTC). After 24 h of incubation in 37 ^{o}C, the triphenyl formazan (TPF) released was extracted with acetone and assayed at 546 nm in UV-VIS spectrophotometer [13]. The global soil hydrolysis activity was evaluated by measuring the activity of fluorescein diacetate hydrolysis (FDAH) as described by Adam and Duncan [14]. After 1 hour of incubation the reaction was stopped by adding the mixture of methyl alcohol and chloroform (1:2). Then the soil suspension was centrifuged at 4000 rev

min^{-1} for 10–15 minutes and the optical density of a coloured end product fluorescein (F) was measured at 490 nm. A fumigation-extraction method was used to estimate microbial biomass C (MBC) and N (MBN) with extractable C and N converted to microbial C and N using standard factors (Vance et al, 1987). Soil was fumigated with ethanol-free chloroform for 24 h. Fumigated and unfumigated soil samples were then extracted with 0.5 M K_2SO_4 for 30 min. Subsamples of filtrates from both fumigated and unfumigated soils were analyzed for extractable C [15] and N [16]. Respiration was determined as described by Stotzky [17]. CO_2 evolved from samples was captured with alkali in $BaCl_2$, the remaining alkali concentration was determined by titration with HCl. Respiration was expressed as CO_2 evolution per gram dry weight and hour ($mgCO_2 \cdot g^{-1} \cdot h^{-1}$). All determinations of microbiological properties were made in triplicate and data were corrected to oven-dry (16 h at 105 ^oC) moisture content.

Soil samples were analyzed for chemical properties after air-drying at room temperature and sieving (< 2 mm). Soil pH in water was measured using the potentiometric method in 1 : 2.5 soil: water suspensions; total organic carbon (TOC) and total nitrogen (TN) contents were determined using a dry combustion CN analyzer (Vario Max CN).

A semivariogrm was determined for each variable to ascertain the degree of spatial variability between neighboring observation, and the appropriate model function was fit to the semivariogram. A semivariogram consists of three basic parameters which describe the spatial structure as: $\gamma(h) = C_0 + C$. C_o represents the *nugget effect*, which is the local variation occurring at scales smaller than the sampling interval, such as sampling error, fine-scale spatial variability and measurement error. $C_0 + C$ is the *sill* (total variance). The distance at which the semivariogram levels off at the sill is called the range [1]. The spatial variability of the properties studied was categorized into classes based on the percentage of total variance present as random variance: $[C_0 / (C_0 + + C)] \cdot 100$, as proposed by [18]. When the ratio was less than 25 %, the variable had a strong spatial dependence; if the ratio was between 25–75 %, the variable had a moderate dependence; otherwise, the variable was considered randomly correlated.

The maps illustrating the spatial variance of the parameters determined were drawn on the basis of the semivariograms. The geostatistical calculations were done using Isatis software (Geovariance Co.).

Results and discussion

The concentration of TOC varied between 13.1 and 25.1 $g \cdot kg^{-1}$ (with mean value 18.7 $g \cdot kg^{-1}$) in April and between 15.2 and 26.5 $g \cdot kg^{-1}$ (mean 19.8 $g \cdot kg^{-1}$) in August. The total nitrogen content ranged from 1.41 to 3.02 $g \cdot kg^{-1}$ in April and from 1.52 to 2.86 $g \cdot kg^{-1}$ in August. The average value of soil pH-H_2O (arithmetic mean) was 7.02 in April and 6.85 in August.

Values for FDAH activity and C and N microbial biomass content studied in April were significantly ($P < 0.05$) greater than those determined in August, while DH activity were statistically insignificant between both sampling dates (Fig. 1a, b). Higher ranges (maximum and minimum) of TN, MBC, MBN concentrations as well as FDAH

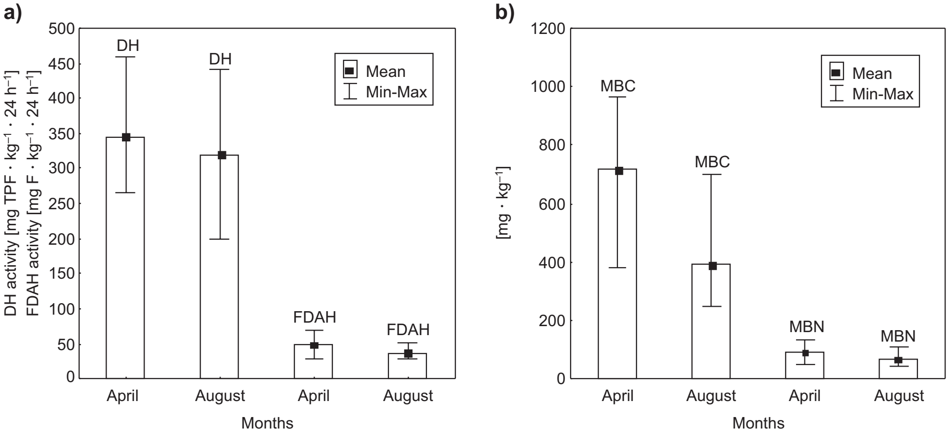

Fig. 1. Basic statistical parameters of variables studied ($n = 50$); DH – dehydrogenase, FDAH – fluorescein diacetate hydrolysis (a), MBC, MBN (b)

activity were shown for data collected in April than in August. The remaining variables were similar for those parameters in case of both sampling dates.

In general, the all data showed spatial dependence. Parameters for semivariogram models are given in Table 1 and Figs. 2, 3.

Table 1

Parameters of variogram models

Property	Month	Model*	Nugget (C_0)	Sill ($C_0 + C$)	$C_0/(C_0 + C)$ [%]	Range [m]	^SD
DH	April August	SF, L SF, L	— —	7102 7237	— —	13 11	— —
FDAH	April August	L, NE SF, L	23.6 —	43.7 13.6	59 —	— 13	M —
MBC	April August	L, NE SF, L	9750 —	12750 13737	76.5 —	— 10	W —
MBN	April August	SF SF	— —	294.2 327	— —	10 17	— —
BR_3	April August	L, NE L, NE	0.231 0.292	0.342 0.410	76.5 71.2	— —	M M

* SF – spherical, L – linear, NE – nugget effect, ^SD – spatial dependence, M – moderate, W – weak; DH – dehydrognase activity [mgTPF · kg^{-1} · 24 h^{-1}], FDAH – fluorescein diacetate salt hydrolysis activity [mgF · kg^{-1}· h^{-1}], MBC – microbial biomass content [mg · kg^{-1}], MBN – microbial biomass content [mg · kg^{-1}], BR_3 – basal respiration after 3 days of incubation [$mgCO_2$ · kg^{-1} · h^{-1}].

Expect BR_3 and MBN, all studied properties displayed differences in spatial structure in April and in August. Semivariograms exhibited a spatial structure that could be best described by spherical model for MBN (Table 1, Fig. 3), by linear model for BR_3 and FDAH activity in April, while spherical/linear models described DH activity, FDAH

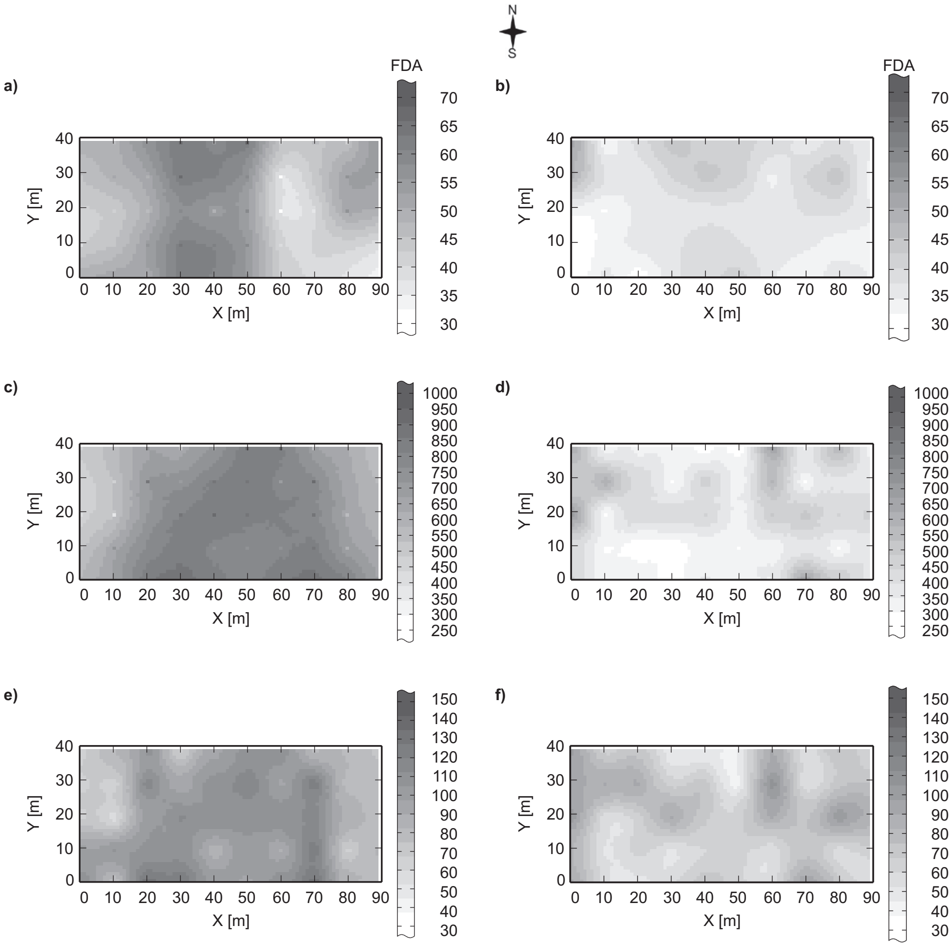

Fig. 2. Spatial distribution of fluorescein diacetate hydrolysis activity (FDAH) in April (a) and in August (b), microbial biomass carbon (MBC) content in April (c) and in August (d) and microbial biomass nitrogen (MBN) concentration in April (e) and in August (f)

activity and MBC content in August. Spatial dependence of BR_3, MBC and FDAH activity in April showed short-range variability represented by nugget effect. Differences in semivariograms parameters between MBC and DH activity may be because DH provides a measure of potential activity of living cells [19] while MBC is a measure of C of microbial origin without distinction among living, dormant and dead microbial cells [20].

To determine the grade of spatial dependence of each property, the *nugget*-to-*sill* ratio from all semivariograms was calculated according to Cambardella et al [18]. Properties studied indicated a moderate (between 25–75 % spatial variability) and a weak spatial variability (above 75 % spatial variability). High (or pure) nugget effect

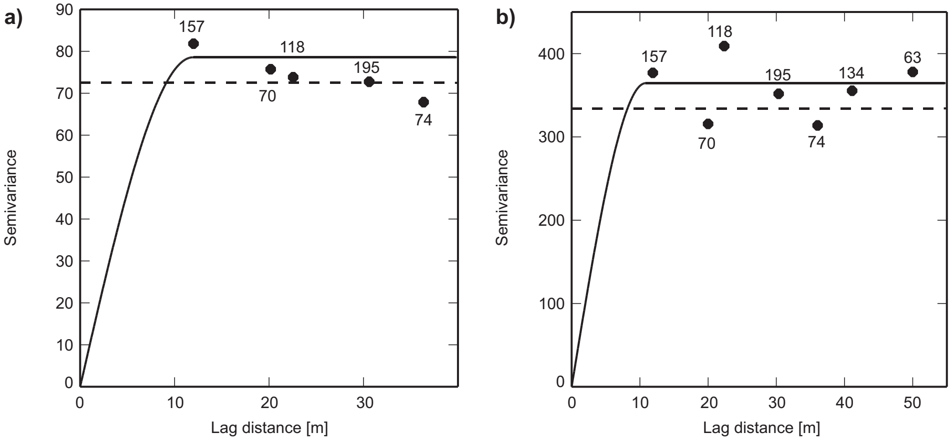

Fig. 3. Experimental semivariograms of microbial biomass nitrogen (MBN) concentration in April (a) and in August (b)

can represent either extreme homogeneity (all points have similar values) or extreme heterogeneity (values are very different, in random way) [3]. It is generally excepted [10, 18] that a weak spatial dependency of soil properties is attributed to extrinsic factors, like farmers' management (*eg* fertilizers application) while a strong spatial dependency is controlled by intrinsic factors, like texture and mineralogy. It was stated that agricultural practices led to a high nugget variance of some soil properties (MBC, MBN, DH activity) and masked detection of spatial structure at the sampling scale used [21].

The ranges of the influence calculated for the microbial properties measured in this study ranged from 10 to 17 m. Since the samples separated by a distance smaller than the range are related spatially [18, 22], the range values of this study showed that all variables were spatially autocorrelated and either the sampling distance (10 m) was suitable. The values of range depend on the sampling area size and sampling design. Cambardella et al [18] found spatial dependency for DH activity at a range of 51 m in a no-till field while Nunan et al [23] showed spatial dependence for that property at the micrometer scale. The ranges of spatial dependence reported for MBC were between 0.3–3.1 m [24–27].

A band of the highest FDAH activity run from north to south part of the field at 30–50 of its length (Figs 2 a, b). Additionally, clearly higher activity of the FDAH was detected in the north-west part of the field. The mode of spatial distribution of FDAH activity was similar in both sampling dates. Kriged maps of MBC and MBN concentrations showed a irregular distribution; the nests of higher results were irregularly found among lower data sets (Fig. 2 c–f). Moreover, the data of those properties showed temporal differentiation, *ie*, they were different in April and August in the same locations. The difference in spatial structure of MBC and MBN content can reflect different spatial distribution of various microbial groups (fungal or bacterial dominance) which could occur in cultivated soils [28, 29].

Conclusions

The part of agriculture field described in this study was originally selected to represent a relatively homogenous system, also in regard to agricultural management. Despite this and a small area sampled (40 × 90 m), a great deal of spatial variability was observed in the properties studied. Some properties (*eg* DH activity and MBN content) were formed only by the structured variance suggesting that the intristic factors (*eg* texture, soil mineralogy) may control the variability of these parameters. Other properties (*eg* BR_3, MBC concentration in April) however revealed that nugget effect/random component was dominant over the structured variability, what pointed that their changeability was influenced by random factors (*eg* measurement error, micronest structures such as irregular fertilization).

Moreover, results confirmed temporal evolution of the spatial structure of properties studied. That is why in order to determine the nature and pattern of soil variability, more than one (seasonal) sampling is needed.

Since the range was bigger or similar to 10 m the sampling distance chosen in the study was suitable. Sampling scheme that involve too few sampling locations will be inadequate for mapping and possible management requirements. In turn, sampling schemes that are too dense may involve high labor and equipment costs, and is undesirable too. Thus, spatial analysis could be useful for developing appropriate sampling strategies.

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ANALIZA GEOSTATYSTYCZNA ZMIENNOŚCI CZASOWO-PRZESTRZENNEJ GLEBOWEJ BIOMASY MIKROBIOLOGICZNEJ I JEJ AKTYWNOŚCI W SKALI POLETKOWEJ

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Abstrakt: W poziomie powierzchniowym (0–20 cm) czarnej ziemi badano zmienność czasowo-przestrzenną zawartości glebowej biomasy mikrobiologicznej (C i N biomasy mikrobiologicznej – MBC i MBN) oraz jej aktywności (aktywność dehydrogenaz – DH, poziom hydrolizy dioctanu fluoresceiny – FDAH oraz oddychanie glebowe – BR_3). W kwietniu i w sierpniu 2007 r. pobrano 50 próbek glebowych z punktów zlokalizowanych w sztywnej siatce kwadratów (10 m × 10 m). Wyniki opracowano metodami geostatystycznymi.

Zmienność przestrzenną badanych parametrów przedstawiono za pomocą sferycznych lub mieszanych (sferyczno-liniowych) modeli semivariogamów, z efektem samorodka (BR_3, FDAH i MBC w kwietniu) lub bez udziału zmienności losowej (DH, FDAH, MBN i MBC w sierpniu).

Poziom oddychania gleby oraz aktywność FDAH (kwiecień) znajdowały się w średniej klasie zmienności (wariancja samorodka pomiędzy 25–75 %), jedynie zawartość MBC w kwietniu znajdowała się w niskiej klasie zmienności (wariancja samorodka < 25 %). Zakresy autokorelacji badanych zmiennych wynosiły od 10 do 17 m. Mapy rastrowe wykazały, że wartości badanych zmiennych były nieregularnie rozmieszczone na badanym obszarze. Ponadto, dla wszystkich badanych cech, z wyjątkiem FDAH, uzyskano odmienne rozmieszczenie przestrzenne wyników w obu terminach analiz.

Słowa kluczowe: zmienność czasowo-przestrzenna, geostatystyka, biomasa mikrobiologiczna, hydroliza FDA, dehydrogenazy, oddychanie gleby

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ABUNDANCE IN MACRONUTRIENTS OF SOILS UNDER VEGETABLE CULTIVATION IN OPEN GROUNDS AND UNDER FOIL TUNNELS

ZASOBNOŚĆ W MAKROSKŁADNIKI GLEB POD UPRAWAMI WARZYW W TUNELACH FOLIOWYCH I W GRUNCIE

Abstract: Production of vegetables and fruits in Poland is most often quite intensive, thus it is basing on introducing into soil large doses of mineral fertilizers, little manuring and without or with the limited crop rotation. Producers of vegetables apply high amounts of fertilizers leading often to their exaggerated accumulation in the soil. The aim of the work was to evaluate the abundance of nutrients, and determine changes in the soil environment resulting from agro-technological treatments applied in the intensive growing of vegetable in foil tunnels and open ground. Results of studies indicated the acidification of soils under the vegetable growing, especially in foil tunnels as a result of intensive mineral fertilizing which have increased the hydrolytical acidity, reducing the share of alkaline cations in the soil sorption complex in comparison with the agriculturally unused soil of the region. In the soil under open ground and foil tunnels vegetable cultivation a decrease of the organic carbon and accumulation of available forms of potassium and phosphorus were observed when comparing with the unused soil. The accumulation of available phosphorus and potassium in the soil under the vegetable cultivation was so significant that it can adversely affect uptaking of other nutrients by vegetables, thus lowered their ability to supply plants with nutrients, as well as affect adversely the environment.

Keywords: vegetable growing, soil reaction, organic carbon, macronutrients

The production of vegetables and fruits in Poland usually is intensive, basing on large doses of mineral fertilizers and without, or with limited manuring and crop rotation [1, 2]. The soil under the vegetable growing is depleted of nutrients taken up with every crop. Their uptake must be compensated with mineral and organic fertilizers. Producers of vegetables, in concern of delivering to the soil appropriate amounts of crop forming elements, introduce into soil exaggerated amounts of fertilizers, causing rather

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their accumulation in the soil than depletion [3]. In field cultivation mineral elements applied in large doses, exceeding the real demand of plants, can undergo surface flows in the result of violent rainfalls, or filtering deep into the soil profile [2, 4, 5]. Applying large doses of fertilizers is also aimed at precipitating cropping which is for the producer the most important since an easiness of the market, a price and a profitability of the production depend on the date of the harvest [3, 6].

The commune Igolomia-Wawrzenczyce is located in the Malopolska province in the Krakow district. It belongs to typically agricultural communes, specializing in the vegetable production, with the long-standing tradition. In its area fertile soils – chernozems – are found determining the intense vegetable growing, which surface of cropping occupies over the half of the arable land of the commune [7].

The purpose of the work was to evaluate abundance in nutrients, and determining changes in the soil environment resulting from agro-technological treatments applied in the intensive vegetable growing in foil tunnels and open ground.

Materials and methods

The commune Igolomia-Wawrzenczyce is located in the distance of about 10 km to the east of Krakow (N50^{o} 07′ , E20^{o} 21′). It is characterized by a wavy, wavy-hilly and flat lie of the land, and in the majority is covered with loess deposits. The average annual temperature is from +6 to +8 ^{o}C, and the sum of rainfalls is of 600 mm a year. Favourable physiographic, lithographic and climatic conditions of the commune and the proximity of markets are supporting the development of the vegetable gardening both in open ground and foil tunnels [7].

For examinations soil material was taken up from 13 objects located in the Igolomia-Wawrzenczyce commune, from the depth of 0–25 cm. From every object 3 individual soil samples were taken. Six objects constituted soils under open ground cropping: of onion (G2 and G3), cauliflower (G4 and G5), cabbages (G6) and celery – G7. Next six objects were soil under foil tunnels cropping of: peppers (T8, T9 and T10), of tomato (T11 and T12) and cucumber (T13). A soil of the extensively used, occasionally mown meadow, described in the work as unused soil constituted the referential object – N1.

In the studied soil material following properties were determined:

– pH values in 1:2.5 solutions of H_2O potentiometrically [8];

– composition of sorption complex through determination of exchangeable Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} cations in the 1 mol · dm^{-3} NH_4Cl solution for non-calcareous soils and in 0.5 mol · dm^{-3} NH_4Cl solution for calcareous soils;

– contents of available forms of phosphorus and potassium with Egner–Riehm's method and magnesium with Schachtschabel's method [8].

Contents of (Ca^{2+}, Mg^{2+}, K^{+} , Na^{+}) exchangeable forms and (P, K, Mg) available forms in obtained in this way solutions were determined with the *spectrometer of atomic emission with inductively induced argon plasma* ICP-AES JY 238 ULTRACE of Jobin Yvon:

– hydrolytic acidity by Kappen's method, using 1 mol · dm^{-3} CH_3COONa [8];

– level of total nitrogen, total and inorganic carbon with the use of automatic analyzer of these elements: TOC-TN 1200 Thermo Euroglas apparatus. The level of organic carbon was calculated as a difference between total and inorganic carbon levels;

– contents of available phosphorus by Olsen method, with the use of 0.5 mol · dm^{-3} $NaHCO_3$ with pH = 8.5 as an extractor. Phosphorous was measured colorimetrically with spectrometer UV-VIS, Aquamate at the wavelength of 720 nm [9].

Statistical analysis of results was carried out with the method of ANOVA unifactor variation analysis in the random arrangement. To estimate the significance of differences between mean values homogeneous groups were appointed using the test *a posteriori* of Fisher. *Standard deviations* (SD) and for some parameters coefficients of *variation* (V %) and values of the Pearson's linear correlation coefficient (r) were calculated. All calculations were performed using the Statistica package v. 10 PL. Graphs were prepared using Excel 2003 package.

Results

Examined soils were derived from loess and they had silty texture. Soil reaction under the open ground vegetable growing and of agriculturally unused soil was slightly acid to neutral, pH values measured in H_2O suspension were placed within the limits of 5.7–7.0. Soils of vegetables tunnel cultivations had acid to slightly acid reaction (pH_{H_2O} 4.8–6.2). Diversification of the pH values of the examined soils resulted from differences in saturation of sorption complex with alkaline cations. In sorption complex of studied soils cations of calcium prevailed. Their participation was associated with the way of soil using, and it was set in the order: unused soil > soil of open ground cultivations > soil of tunnel cultivations and on average it took out appropriately 82.9, 76.7 and 68.2 %, when differences in saturation of sorption complex with discussed cation between the unused soil and the soils under the vegetable growing were statistically significant (Table 1, Fig. 1).

Average participation of cations of magnesium in sorption complex was set inversely towards the participation of cations of calcium that is: soils of tunnel cultivations > soils of open ground cultivations > unused soil, and took out appropriately: 11.4, 9.1 and 8.4 %. Statistically significant differences appeared between the average participation of Mg cations in sorption complex in soils of open ground and tunnel vegetables. Participation of sodium and potassium cations in sorption complex of discussed soils were not statistically significantly diversified in relation to the way of soil use and was located in a limit appropriately: 1.2–2 % and 0.6–2.5 % (Table 1, Fig. 1). However a participation of the hydrolytic acidity in the capacity of sorption complex in soils of tunnel cultivations (16 %) was statistically significantly greater comparing with the soil of open ground cultivations (10 %) and of unused soil (6.8 %) (Fig. 1).

The way of using affected also the accumulation of organic carbon and total nitrogen in the examined soils. Indicated average contents of these elements placed in the order: unused soil > soils of tunnel cultivations > soils of open ground cultivations, differences in C and N contents between soil from the open ground and tunnel cultivations of vegetables were small. In spite of intensive fertilizing in the soils under vegetable

Table 1

Values of pH and sorption properties of studied soils (arithmetic mean of three individual samples ± standard deviation)

Soil	pH H_2O	Exchangeables cations mmol(+)/kg soil				Ha**	CEC***
		Ca^{2+}	Mg^{2+}	K^+	Na^+	mmol(+)/kg soil	
N1*	6.6	141.7 ± 0.1	14.4 ± 0.6	1.10 ± 0.08	2.02 ± 0.02	11.6 ± 0.2	170.9 ± 0.1
Open ground vegetable cultivation							
G2	5.7	79.0 ± 0.1	12.8 ± 0.2	1.04 ± 0.04	2.96 ± 0.03	19.5 ± 0.5	115.4 ± 0.1
G3	6.1	99.8 ± 0.9	9.94 ± 0.02	0.86 ± 0.03	1.33 ± 0.07	13.5 ± 0.3	125.5 ± 0.4
G4	5.9	114.8 ± 0.4	7.65 ± 0.02	2.27 ± 0.08	2.76 ± 0.01	15.6 ± 0.7	143.2 ± 0.1
G5	6.2	86.6 ± 0.7	16.1 ± 0.1	4.79 ± 0.05	1.57 ± 0.01	18.4 ± 0.1	127.5 ± 0.1
G6	7.0	113.8 ± 0.6	13.9 ± 0.3	4.12 ± 0.02	1.42 ± 0.02	6.76 ± 0.06	140.0 ± 0.2
G7	7.0	117.5 ± 0.2	12.3 ± 0.2	6.61 ± 0.03	3.39 ± 0.01	6.24 ± 0.01	146.0 ± 0.9
Foil tunnels vegetable cultivation							
T8	4.8	49.5 ± 0.2	11.2 ± 0.1	1.21 ± 0.02	0.73 ± 0.08	61.1 ± 0.2	123.8 ± 0.2
T9	5.7	80.9 ± 0.3	13.9 ± 0.1	1.32 ± 0.02	1.98 ± 0.04	21.7 ± 0.1	119.8 ± 0.1
T10	6.3	143.7 ± 0.2	20.5 ± 0.2	1.24 ± 0.07	2.56 ± 0.02	17.4 ± 0.3	185.4 ± 0.4
T11	6.1	85.7 ± 0.1	11.2 ± 0.2	6.00 ± 0.01	4.38 ± 0.01	17.6 ± 0.3	124.9 ± 0.1
T12	6.4	146.3 ± 0.3	19.6 ± 0.2	4.23 ± 0.06	3.41 ± 0.03	11.8 ± 0.3	185.3 ± 0.5
T13	6.2	127.9 ± 0.7	29.6 ± 0.2	8.17 ± 0.01	5.32 ± 0.05	19.1 ± 0.3	190.2 ± 0.6

* N1 – unused soil, G2 and G3 – onion open ground growing, G4 and G5 – cauliflower open ground growing, G6 – cabbage open ground cultivation, G7 – celery open ground cultivation, T8, T9 and T10 – pepper foil tunnel cultivation, T11 and T12 – tomato foil tunnel cultivation, T13 – cucumber foil tunnel cultivation; ** Hydrolytical acidity; ***CEC – cation exchangeable capacity.

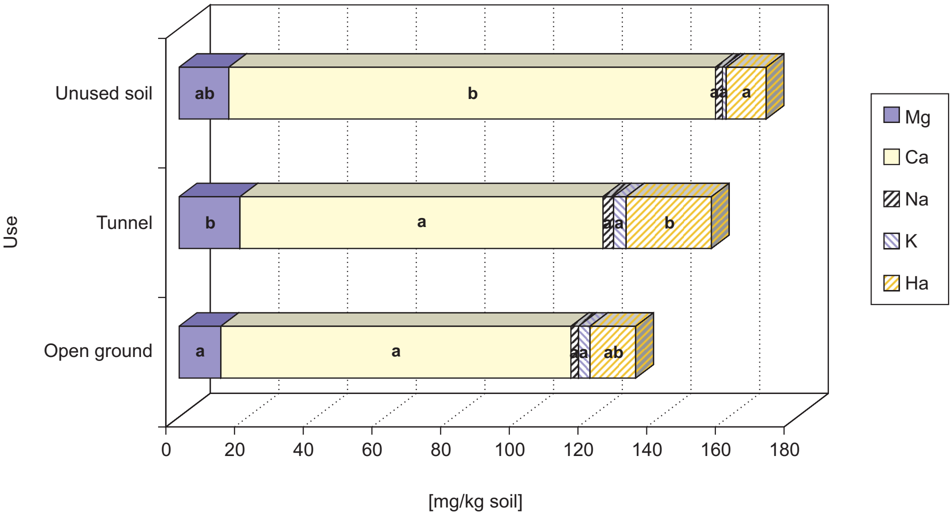

Fig. 1. Mean composition of sorption complex of differently used soil, the same letters mean the lack of statistically significant differences at the significance level $\alpha \leq 0.05$

growing the accumulation of organic carbon and total nitrogen were appropriately 2-fold and about 1.5-fold lower than in the unused soil, the last one was characterized by a little bit broader average C : N ratio (12.3), comparing with the soil of the vegetable growing, in which it took out about 10 (Table 2).

Intensive vegetables fertilizing influenced the accumulation of available forms of phosphorus and potassium in the soil under their crops in the strongest way. Average content of available phosphorus determined with Egner-Riehm's method in the unused soil was definite in "Materials worked up for fertilizer recommendations on arable lands" [10] as very low, and in the soil from the vegetable growing: open ground and tunnel, as very high, a little bit higher in the soil under tunnels than open ground cultivation but this difference was statistically insignificant (Table 2, Fig. 2). Statistically significantly lower was indeed an average content of phosphorus, extracted with $NaHCO_3$ (Olsen's method) in the unused soil when comparing with the soil, in which vegetables were growing. Average contents of this element determined with Olsen's method in the soil from open ground and tunnel cultivations of vegetables, amounted to appropriately: 248.3 and 228.6 mg P_2O_5/kg of the soil. Average amounts of phosphorus extracted with solution of the calcium lactate (with method of Egner–Riehm) from the soil of the vegetable growing were about 3-fold higher than extracted with $NaHCO_3$ (Olsen's method), while in the unused soil contents of phosphorus extracted with both reagents were identical and amounted about 43 mg P_2O_5/kg of the soil. Average contents of available potassium extracted with the calcium lactate from the soil under vegetable growing were very high [10] and statistically significantly higher than in the unused soil, in which the low content of this element was determined. Agro-technological treatments applied at the vegetable growing did not affect the content of

Table 2

Selected chemical properties of studied soils (arithmetic mean of three individual samples ± standard deviation)

Soil	C	N	C:N	MgO	K_2O	P_2O_5	Olsen-P_2O_5
	[g/kg]			[mg/kg]			
N1*	31.4 ± 0.9	2.31 ± 0.07	13.5	220.0 ± 1.7	85.1 ± 0.0	43.2 ± 4.3	43.5 ± 0.6
Open ground vegetable cultivation							
G2	12.9 ± 0.1	1.4 3± 0.03	9.0	244.2 ± 5.8	109.8 ± 2.3	387.1 ± 3.2	345.5 ± 1.3
G3	21.3 ± 2.2	1.47 ± 0.02	14.5	174.2 ± 2.5	97.7 ± 3.7	108.8 ± 0.3	282.1 ± 2.0
G4	11.3 ± 0.1	1.50 ± 0.06	7.5	143.3 ± 6.6	219.8 ± 3.5	602.6 ± 37.4	195.7 ± 2.0
G5	11.9 ± 0.5	1.60 ± 0.10	7.4	240.0 ± 1.6	568.3 ± 2.3	728.1± 23.3	201.3 ± 1.3
G6	16.7 ± 0.2	1.48 ± 0.04	11.3	206.7 ± 15.0	510.9 ± 3.3	968.4 ± 46.2	219.7 ± 2.1
G7	18.7 ± 0.1	1.51 ± 0.03	12.4	180.0 ± 1.6	860.9 ± 13.3	1077.6 ± 95.5	245.1 ± 1.0
Foil tunnels vegetable cultivation							
T8	16.1 ± 0.4	1.65 ± 0.06	9.8	190.8 ±1 0.8	159.3 ± 1.6	528.3 ± 15.3	154.7 ± 1.1
T9	11.7 ± 0.4	1.50 ± 0.10	7.8	169.3 ± 0.9	358.2 ± 9.4	1137.2 ± 17.7	253.4 ± 3.4
T10	16.6 ± 0.4	2.10 ± 0.08	7.9	315.0 ± 6.6	99.2 ± 0.7	151.3 ± 7.5	118.5 ± 0.8
T11	13.9 ± 0.1	1.80 ± 0.09	7.7	160.0 ± 1.6	731.5 ± 12.5	1308.2 ± 99.8	262.6 ± 2.2

* See explanation under Table 1.

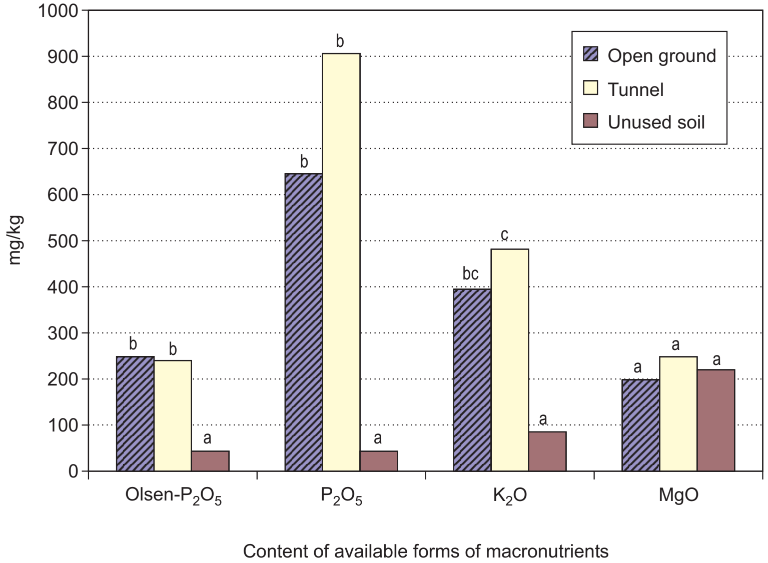

Fig. 2. Mean content of macronutrients in examined soils of different use, the same letters mean the lack of statistically significant differences at the significance level $\alpha \leq .05$

available magnesium, in all examined soils very high contents of this element were indicated and differences between contents of this form of magnesium extracted from the differently used soils were statistically insignificant (Table 2, Fig. 2).

Discussion

In Poland in the last years the area of vegetable growing under covers have reduced, while harvests of vegetables cultivated under protections have slowly but systematically grown [1, 2, 11]. Extremely crucial factor in the production of vegetables is an appropriate supplying with nutrients. Vegetables belong to cultivations with high nutritional requirements, especially with reference to phosphorus and potassium. These needs of plants are satisfied mainly with mineral fertilizers, applied in large doses. The accumulation of macroelements in parts of edible vegetables is determined by their presence in the soil in forms available to plants. Correctly run production, even intensive, in compliance with agro-technological principles should not lead to the decline of the soil. Nevertheless there are often made mistakes leading to the decrease of qualities of crops and of soil production capacities or threatening the environment [3, 6].

Agro-technological treatments, applied in the vegetable growing contributed to changes of physical and chemical properties of examined soils comparing with the unused soil located in the same region. These changes consisted above all in the considerable accumulation of some nutrients in the soil under the vegetable growing, often in amounts exceeding the demand of plants. Amounts of phosphorus and available potassium determined with Egner-Riehm's method exceeded very much recommended contents of this element in the soil under growing of given vegetable. Contents of phosphorus in case of the soil, from the tunnel cultivation of the cucumber were above 3-fold higher than contents recommended by Chemical-Agricultural Stations for the cultivation of this vegetable under tunnel, that is they crossed the border of harmfulness [6]. As such it is regarded the content of the given element twice as bigger than recommended [6]. However the excess of phosphorus and potassium are not directly harmful for plants, their exaggerated accumulation in soils hinders taking up of other nutrients and plants can manifest the deficiency of other elements. Contents of available phosphorus extracted with both solutions: the calcium lactate and the acid calcium carbonate were strongly positively correlated with the content of exchangeable and available potassium, Pearson's coefficients of simple correlation took out appropriately 0.81 and 0.50 (exchangeable potassium) and 0.88 and 0.53 (available potassium), ($\alpha < 0.05$) which proves the intensive fertilizing with these elements. Content of phosphorus determined with Olsen's method in the examined soils under vegetable growing in all cases exceeded a threshold value (100 mg P_2O_5/kg of the soil) determined as one of criteria of the hortic horizon. Appearing of this horizon indicates an advanced anthropogenic processes going on in the soil [12].

The exaggerated content of phosphorus can have also negative environmental effects associated with phosphorus getting to waters. Examinations conducted in the Research Rothamsted Station in Great Britain indicated significant increasing in the content of phosphorus in drainage waters to above 2 mg/dm^3, when content of determined phosphorus with Olsen's method crossed 60 mg P/kg (274 mg P_2O_5/kg) [4]. In the examined soils of open ground and tunnel vegetable cultivation the content of this element in some cases was close or even exceeded this amount.

There was not ascertained, expected, significant relation between pH values of the soil and the content of available phosphorus extracted with both methods Egner-Riehm's ($r = 0.048$, $\alpha > 0.05$) as well as Olsen's (-0.005, $\alpha > 0.05$). The fact can be explained by the low changeability of pH among the examined soils. The variation coefficient amounted to 8.61 %. Besides the content of available phosphorus was undoubtedly connected with a high inputs of this element into the soil and not fully taken up by plants [13].

Changes of physical and chemical properties of soils under the vegetable growing, resulting from conducted agro-technological treatments particularly intensive fertilizing, such as a decrease in the content of organic carbon and accumulation of phosphorus and potassium, were observed in soils of both the open ground and under foil tunnel vegetable cultivations. Moreover in soils of tunnel cultivations of vegetables a decrease in the pH values was also noticeable. Similar effects of intensive mineral fertilizing Lin et al [14] have observed in the soil under the vegetable growing in plastic tunnels in north China. According to Authors' the long-term vegetable growing in tunnels in the monoculture can lead to the increase of the soil acidity, when exaggerated accumulations of nutrients influences negatively a biological soil life and in consequence leads to lowering of its fertility.

Conclusions

1. Intensive applying of mineral fertilizers into soils under the vegetable growing, especially under foil tunnels increased the soil hydrolytical acidity, by reducing the participation of alkaline cations in sorption complex and finally acidified soils.

2. In the soil of open ground and tunnel vegetable cultivations a lowered content of organic carbon and accumulation of available forms of phosphorus and potassium were observed in comparison with the unused soil.

3. The accumulation of available phosphorus and potassium in soils under the vegetable growing is so high that it can adversely affect taking of other nutrients by vegetables, thus lower their ability to supply plants with nutrients, as well as pose environmental problems.

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ZASOBNOŚĆ W MAKROSKŁADNIKI GLEB POD UPRAWAMI WARZYW W TUNELACH FOLIOWYCH I W GRUNCIE

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Abstrakt: Produkcja warzyw i owoców w Polsce ma najczęściej charakter intensywny, czyli polega na wprowadzaniu do gleby dużych dawek nawozów mineralnych, niewielkim nawożeniu nawozami organicznymi i bez lub z ograniczonym płodozmianem. Producenci warzyw wprowadzają do gleb duże ilości nawozów, prowadząc często do ich nadmiernej akumulacji w glebie. Celem pracy było ocena zasobności w składniki odżywcze oraz określenie zmian właściwości środowiska glebowego zachodzących na skutek zabiegów agrotechnicznych stosowanych w intensywnej uprawie warzyw w tunelach foliowych i gruncie. Rezultaty przeprowadzonych badań wskazały na zakwaszenie gleb pod uprawą warzyw, szczególnie w tunelach foliowych w wyniku intensywnego nawożenia mineralnego, w efekcie którego wystąpiło zwiększenie kwasowości hydrolitycznej, zmniejszenie udziału kationów zasadowych w kompleksie sorpcyjnym tych gleb w porównaniu z glebą nieużytkowaną rolniczo tego regionu. W glebach upraw gruntowych i tunelowych warzyw zaobserwowano również zmniejszenie zawartości węgla organicznego i nagromadzenie przyswajalnych form fosforu i potasu w porównaniu do gleby nieużytkowanej. Akumulacja fosforu i potasu przyswajalnego w glebach pod uprawą warzyw była tak znaczna, że może mieć niekorzystny wpływ na pobieranie innych składników pokarmowych przez warzywa, a zatem obniżyć ich zdolność do zaopatrywania roślin w składniki pokarmowe, a także niekorzystnie wpływać na środowisko.

Słowa kluczowe: uprawa warzyw, odczyn gleb, węgiel organiczny, makroskładniki

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DYNAMICS OF ARACHNID OCCURRENCE IN SOIL CONTAMINATED WITH PETROL, DIESEL FUEL AND ENGINE OIL DURING BIOREMEDIATION PROCESS

DYNAMIKA WYSTĘPOWANIA PAJĘCZAKÓW W GLEBIE SKAŻONEJ BENZYNĄ, OLEJEM NAPĘDOWYM I OLEJEM SILNIKOWYM W TRAKCIE PROCESU BIOREMEDIACJI

Abstract: The research aimed at investigating the effect of oil derivatives during the process of their bioremediation on dynamics of arachnid (Arachnida) occurrence. The following objects were established in two series (with bioremediation and without bioremediation): control – unpolluted soil; soil polluted with petrol; soil polluted with diesel fuel and soil polluted with used engine oil (dose: 6 000 mg of fuel $\cdot$ kg^{-1}d.m. of soil). Epigeal fauna was trapped using Barber's traps. The traps were emptied once a week from June to October 2010. Moreover, once a month soil samples were collected from the 0–20 horizon and then examined for arachnid presence in a laboratory under a binocular.

Soil contamination with petrol, diesel fuel and used engine oil leads to drastic reduction of arachnid occurrence in the topsoil layer but is does not negatively affect soil surface penetration by these invertebrates. Some of the applied polluting substances, *eg* used engine oil, petrol even stimulated Arachnida occurrence on the soil surface. Bioremediation did not influence significantly total arachnid occurrence in soil for the period of 5 months since it was conducted. The marked decrease in the number of arachnids was observed in bioremediated topsoil layer while comparing with not bioremediated one during two months after petroleum contamination.

Keywords: oil derivatives, soil, bioremediation, Arachnida

Research conducted so far on the effect of pollutants on arachnid occurrence focused mainly on the influence of heavy metals [1–5], air pollution or chemical plant protec-

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tion [6, 7]. Only few investigations concerned the effect of oil derivatives on this invertebrate group [8–11]. Results of these experiments point to a reduction of species richness and numbers, but also show a considerable diversification of the responses depending on the pollution level in the analyzed environment and the sampling method.

Applied bioremediation, using biopreparations containing specially selected groups of microorganisms, to the ground polluted with oil derivatives allows to accelerate considerably the process of oil derivatives decomposition. Subsequent stages of this process and intermediates which appear at that time may affect both epigeal and soil fauna.

The work aimed at investigating the effect of oil derivatives during the process of their bioremediation on dynamics of arachnid (Arachnida) occurrence.

Material and methods

The experiment was conducted at the Experimental Station of the University of Agriculture in Krakow situated in Mydlniki near Krakow, on agricultural land (covered by low herbaceous vegetation, mainly grass cut twice during vegetation season). The experiment was set up in autumn 2009 using randomised block method in four replications. The indigenous soil was placed in 1 m^3 (1 m × 1 m × 1 m) containers specially adapted for this purpose, and the natural soil layer arrangement was preserved. The containers were placed into the ground so that their upper ridges were level with the soil surface, so they did not pose a barrier for the analyzed invertebrates. Additionally the upper section of the container sides was perforated to allow the invertebrates a free penetration of polluted soil. Once the soil in the containers returned to its natural density and biological fitness, *ie* in June 2010, it was artificially polluted (by pouring onto the surface) with the following oil derivatives: petrol, diesel fuel and used engine oil in the amount corresponding to 6 000 mg of fuel $\cdot$ kg^{-1} d.m. of soil, which was a typical concentration of oil derivatives occurring in a medium polluted soils. A week after the soil contamination, half of the containers were subjected to bioremediation by means of ZB-01 biopreparation designed for biodegradation of oil derivatives, containing selected procaryotic microorganisms revealing high catabolic activity towards the oil derivatives. The following objects were established in each analyzed series: control – unpolluted soil; soil polluted with petrol; soil polluted with diesel fuel and soil polluted with used engine oil. Considering the pollutant content, the process of bioremediation was monitored using extraction-gravimetry on Soxhlet apparatus. Epigeal fauna was trapped using Barber's traps (a 0.9 dm^3 jar dug in level with the ground surface and covered against rainfall water by a plastic roof) placed in the central part of each container. The traps were emptied once a week from June to October 2010. Moreover, once a month soil samples were collected from the 0–20 horizon and then examined for arachnid presence in a laboratory under a binocular. Statistical computations were conducted using Statistica 9.0 PL programme. Means were differentiated using LSD Fisher test on significance level $\alpha = 0.05$.

Results and discussion

Soil contamination with oil derivatives contributed to a drastic reduction of arachnid representative occurrence in the analyzed soil samples (Fig. 1). Only after 3–4 months single Arachnida were spotted in the object contaminated with petrol (both in the bioremediated series and without bioremediation) and used engine oil. Early result of used pollutants towards the tested invertebrates was undoubtedly connected with their lethal effect. In a longer perspective also the effect of oil derivatives on vegetation as a source of food for the investigated mezofauna might have been also important. In the initial period, applied oil derivatives caused almost total destruction of vegetal cover in the studied area. In the course of time (several months later) plant started to reappear, first on petrol polluted soil (both subjected to bioremediation and non-remediated). Cebron et al [9] emphasize the effect of vegetation on the occurrence of soil Arachnida. In the research of these authors on the use of various kinds of bioindicators for the assessment of biological activity in both PAH-polluted and thermal desorption treated soils, the presence of vegetation was the basic factor modifying the number of soil Arachnida. Considerably reduced occurrence of arachnids in soil samples collected from seasonally flooded stream banks polluted with oil derivatives were registered by Couceiro et al [8].

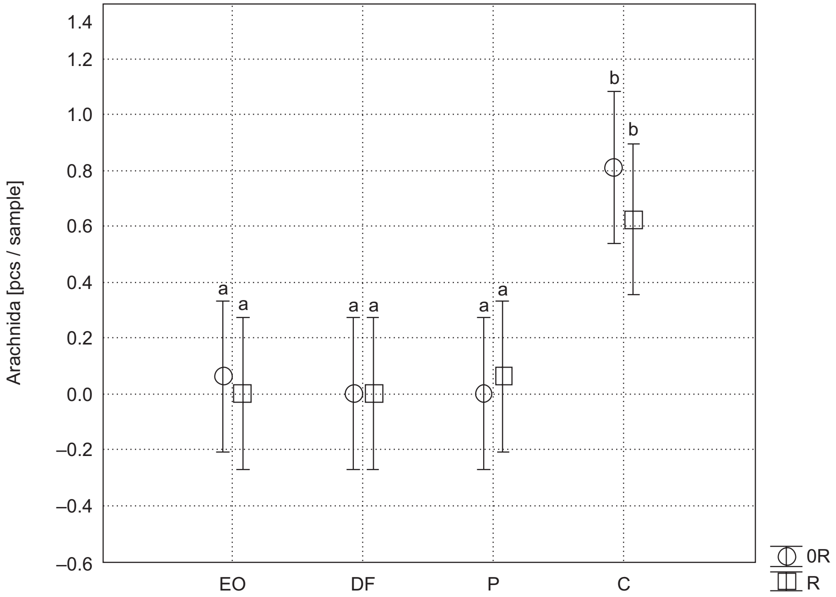

Fig. 1. Occurrence of arachnids in soil samples, average for the investigated period. EO – soil contaminated with used engine oil, DF – soil contaminated with diesel fuel, P – soil contaminated with petrol, C – unpolluted soil, 0R – series without bioremediation, R – series with bioremediation. Means marked with the same letters do not differ significantly according to LSD test at $\alpha = 0.05$; factors contamination x remediation. ⌶ Mean ± 0.95 confidence interval

Among the fauna caught using Barber's traps, arachnids occurred in greatest numbers in the initial period of the experiment, *ie* at the turn of June and July (Fig. 2).

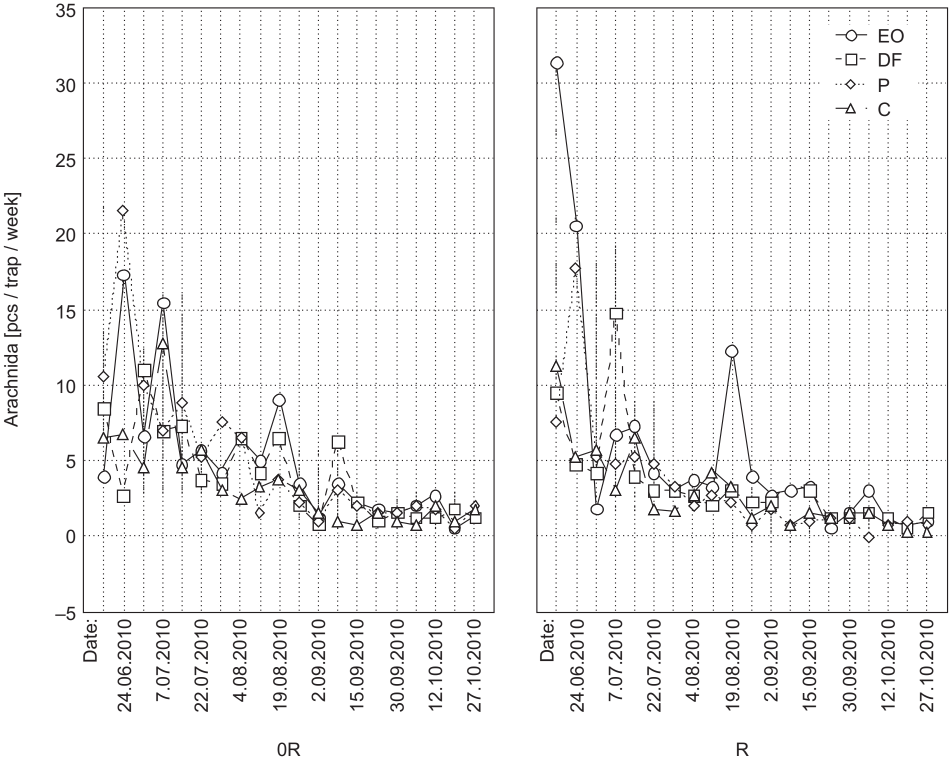

Fig. 2. Course of dynamics of Arachnida occurrence trapped using Barber's traps. The symbols as in Fig. 1

Later their number was several times lower. No such distinct differences in the course of their occurrence dynamics depending on soil contamination were noticed, as in case of arachnids observed in soil samples (Fig. 3). Statistical analysis of data from the subsequent months passing from the moment of soil pollution did not reveal any negative effect of the applied substances on Arachnida presence on soil surface. In some months greater numbers of these invertebrates were even trapped in the contaminated than in the control soil. Also the applied bioremediation did not significantly affect Arachnida occurrence for most of the investigated period. Only during the second month after contamination a marked decline in the number of trapped arachnids was registered in conditions of soil contaminated with petrol in the series with bioremediation. At that time it was similar as noted in the control. During that period a decrease from 4288 to 2841 mg of fuel · kg^{-1} d.m. was observed in the compounds extracted by petroleum spirit. It might have been connected with the stage of intensive bioremediation of soil polluted with petrol, during which short chained intermediates appear, toxic for Arachnida. During a later period of bioremediation a decline in toxic

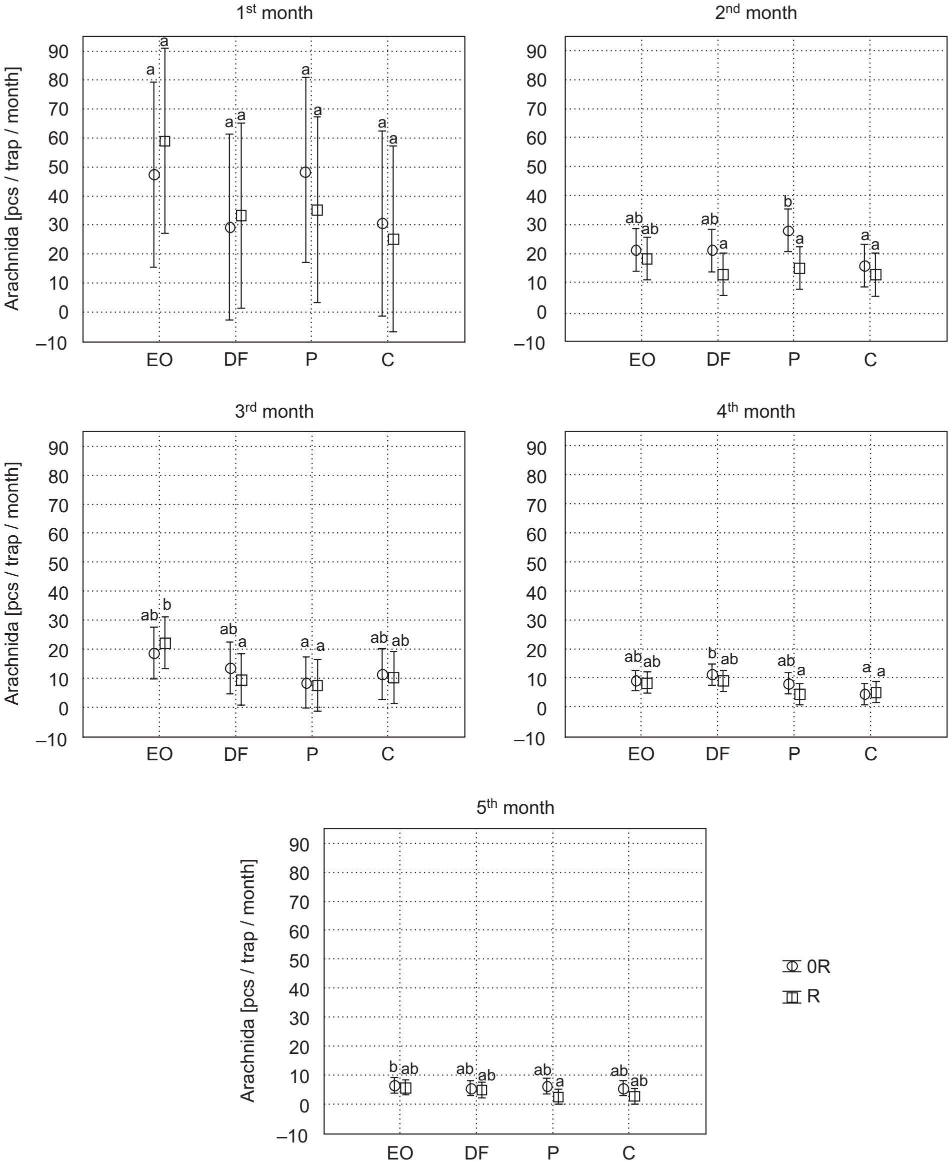

Fig. 3. Occurrence of Arachnida trapped using Barber’s traps in individual months after soil contamination. The symbols as in Fig. 1. Means marked with the same letters do not differ significantly according to LSD test at $\alpha = 0.05$; factors contamination x remediation. ⌶ Mean ±0.95 confidence interval

compounds in soil contaminated with petrol and engine oil and increase in the concentrations of emulsifying compounds and bacteria number were the factors causing an increase in the number of trapped Arachnida. On average during the period of the experiment a significantly higher number of trapped arachnids were noted in the object

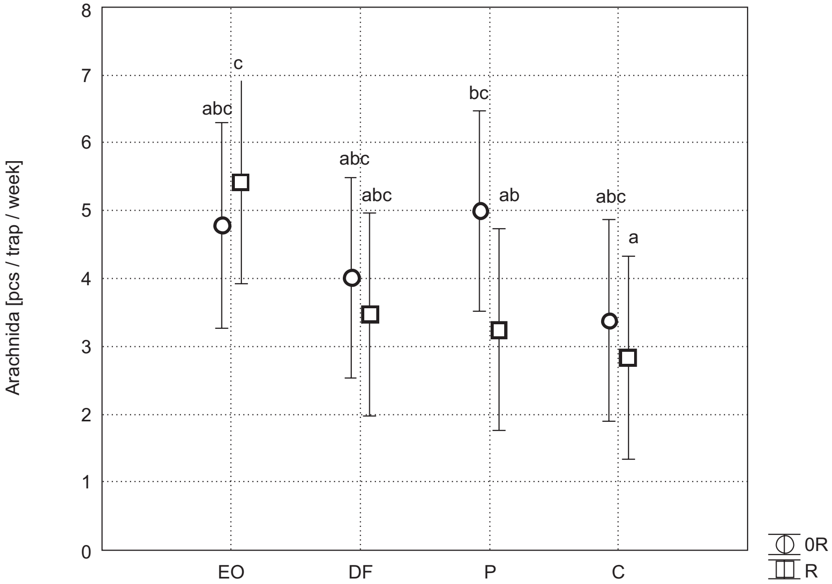

Fig. 4. Occurrence of Arachnida trapped using Barber's traps mean during experiment. The symbols as in Fig. 1. Means marked with the same letters do not differ significantly according to LSD test at $\alpha = 0.05$; factors contamination x remediation. ⌶ Mean ±0.95 confidence interval

where soil was polluted with engine oil and subjected to bioremediation and in the object with petrol contaminated soil than in conditions of clean soil where the biopreparation was applied (Fig. 4). In the Author's previous research [11] on the effect of environmental pollution with oil derivatives in result of a serious road accident on epigeal fauna, no negative effect of them on representatives of Arachnida phylum was noticed, either. Periodically greater number of these invertebrates were trapped in the polluted area. No negative effect of petrol or engine oil applied in a dose of 2 dm^3/m^2 on the number of trapped arachnids penetrating the earth surface was noted [12]. It is interesting to observe, that the area of soil polluted with used engine oil was penetrated by Arachnida irrespectively of the bioremediation, but also their occurrence was more numerous in comparison with the control. These results suggest that composition of engine oil contains attractants for these organisms. The period of time for bioremediation of soil polluted with engine oil was relatively short and pollution level in the topsoil decreased from 36417 to 20608 $mg \cdot kg^{-1}$ d.m. in the investigated period. The result mentioned above stimulates further research on the identification of the substances contained in the oil as stimulants for settling soil surface by this group of organisms.

Conclusions

1. Soil contamination with petrol, diesel fuel and used engine oil leads to drastic reduction of arachnid occurrence in the topsoil layer but is does not negatively affect soil surface penetration by these invertebrates.

2. Some of the applied polluting substances (used engine oil, petrol) even stimulated Arachnida occurrence on the soil surface.

3. Applied bioremediation did not influence significantly total arachnid occurrence in soil for the period of 5 months since it was conducted.

4. Bioremediation of soil polluted with petrol two months after it was conducted contributed to limited presence of Arachnida on the soil surface to the level similar as in the conditions of unpolluted soil.

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DYNAMIKA WYSTĘPOWANIA PAJĘCZAKÓW W GLEBIE SKAŻONEJ BENZYNĄ, OLEJEM NAPĘDOWYM I OLEJEM SILNIKOWYM W TRAKCIE PROCESU BIOREMEDIACJI

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Abstrakt: Celem pracy było zbadanie oddziaływania substancji ropopochodnych w trakcie procesu bioremediacji gleby na dynamikę występowania pajęczaków (Arachnida). W każdej z dwóch serii badawczych (z bioremediacją i bez bioremediacji) utworzono następujące obiekty: 1. kontrola – gleba niezanieczyszczona. 2. gleba sztucznie zanieczyszczona benzyną, 3. gleba sztucznie zanieczyszczona olejem napędowym, 4. gleba sztucznie zanieczyszczona zużytym olejem silnikowym (dawka 6 000 mg paliwa · kg^{-1} s.m. gleby). Odłowy fauny naziemnej prowadzono z wykorzystaniem pułapek Barbera. Pułapki opróżniano raz w tygodniu w okresie od czerwca do października 2010 roku. Ponadto raz w miesiącu pobierano próbki gleby z poziomu 0–20 cm, które następnie przeglądano w laboratorium pod binokularem, pod kątem obecności pajęczaków.

Skażenie gleby benzyną, olejem napędowym i zużytym olejem silnikowym powoduje drastyczne ograniczenie występowania pajęczaków w powierzchniowej warstwie gleby, natomiast nie wpływa negatywnie na penetrację powierzchni gleby przez te bezkręgowce. Niektóre z zastosowanych substancji zanieczyszczających (zużyty olej silnikowy, benzyna) odziaływały wręcz stymulująco na występowanie pajęczaków na powierzchni gleby. Zastosowana bioremediacja, przez okres 5 miesięcy od momentu jej przeprowadzenia, nie wpłynęła istotnie na występowanie pajęczaków ogółem w glebie. Bioremediacja gleby zanieczyszczonej benzyną po upływie dwóch miesięcy od jej przeprowadzenia przyczyniła się do ograniczenia występowania pajęczaków na powierzchni gleby do poziomu podobnego jak w warunkach gleby niezanieczyszczonej.

Słowa kluczowe: ropopochodne, gleba, bioremediacja, Arachnida

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ASSESSMENT OF EFFICIENCY OF HUMIC ACIDS EXTRACTION PROCESS USING DIFFERENT FINENESS OF LIGNITE

OCENA WYDAJNOŚCI EKSTRAKCJI KWASÓW HUMINOWYCH Z WĘGLI BRUNATNYCH O RÓŻNYM UZIARNIENIU

Abstract: Humic acids are a group of distinctive organic compounds, which are created in complicated biochemical processes, such as oxidation, condensation and polymerization of high-molecular products of plant and animal residue decomposition. They facilitate plants micronutrient uptake, improve soil structure, porosity and consequently aeration, water retention and also viscosity, firmness and creating aggregate structures. The aim of the research was to determine efficiency of humic acids extraction process, using different kinds and fineness of lignite. Stronger fines size reduction provides growth of active surface subjected to extractant treatment and better porosity of mass subjected to extraction, so as the lignite fineness decreasing the increase of efficiency of humic acids production is expected. Finding optimum fineness, which is a compromise between extraction efficiency and raw material grinding costs, will enable economical production of humic acids fertilizer agents.

Keywords: humic acids, extraction process efficiency, fineness

Organic substances in soil undergo continuous transformations. Their kind and intensity depends on flora, soil fauna, microorganisms and other physical and chemical properties. Two main directions of changes, which organic matter is subjected to, are mineralization and humification. In fertilizer point of view, the most interesting are reactions that lead to formation of humus compounds, which fulfill a very important role in soil, because they influence on many of its properties like fecundity and productivity. Only 20–25 % of organic matter undergo this kind of transformations and they are much more complicated than matter mineralization process. Humification is based on decay and synthesis of organic compounds as well as polymerization and

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condensation of forming products. This process is not fully explored, because of its complexity. Humus created in this way mainly consists of *humic acids* (HA), *fulvic acids* (FA) and humins. Fulvic acids are soluble in water independently of reaction and characterized by yellow or brown and yellow colour. Humins are black and completely insoluble in water. However, the most interesting, in fertilizer point of view, are humic acids which are dark-brown or black humus fraction insoluble in acidic environment [1–3].

Humic acids are polymers built of aromatic core containing phenol or nitrogen in cyclic form. The core binds with sugars, peptides, amino acids, acids and other aliphatic compounds [1, 2]. Their complex, condensed, irregular and amorphous structure results in chemical and biological decomposition resistance [3, 4]. The majority of widely accepted theories claim that humic acids are high-molecular polymers but the newest researches indicate that this structure consist of low-molecular compounds creating very big associated molecules. This theory does not stand in contradiction to earlier, commonly accepted view. It only suggests that humic acids are not built of regularly repeated monomeric units that form polymer, but miscellaneous molecules physically connected with each other into irregular structure [3, 4].

Use of humic acids

Humic acids have many applications, among others, as dyes, wood hardening agents and they are also used in veterinary medicine or synthetic polymers production [5]. However, they are used the most commonly in agriculture, because of their colloidal character and huge active surface giving them fine adsorptive properties [6]. In natural environment, humic acids mould proper structure of soil, facilitating water retention, improving porosity and consequently aeration. Moreover, the dark colour of humic acids influences on substratum albedo, helping to absorb adequate amount of solar radiation. Adsorptive features also allow to supply necessary micro- and macronutrients to plants and eliminating from the ground ionic and molecular impurities in the form of heavy metals [6–10].

Sources of humic acids

The above-mentioned properties are extremely attractive for fertilizer industry, because process of creating humus in soil lasts incredibly long. In favourable conditions forming 1 cm^3 of humus takes even a few hundred years, while its influence on the ground fertility is inestimable. That is why new sources of humic acids are prospected. For instance, brown coal, peat, biomass, some kinds of soils or even marine sediments are used [11]. One of the richest source of humic compounds are leonardites, an intermediate form between peat and lignite. However, access to their deposits is quite limited, because they occur mainly in the United States of America and that is why other raw materials are usually used. There are many ways of obtaining humic acids. Some of them are based on underground extraction of humic acids using particular microorganisms, but the vast majority includes mining the material and industrial extraction. Using brown coal for that purpose may be very perspective direction. This fossil fuel, because of its dampness, volatile matter and sulfur compounds content influences very unfavorably on the atmosphere during combustion. More especially as in many countries this coal is used almost entirely in power industry. Admittedly the structure of humic compounds depends on bioclimatic conditions in which they were formed, yet there are no significant differences between humus created in soil and this one from coal [6–12].

Influence of chemical and physical factors on humic acids extraction process

Obtaining humic acids from a lignite or some other sources is possible thanks to specific properties of humic compounds, that is their solubility. Humins are insoluble in the whole pH range. Therefore, adding alkaline extractant to the raw material, mixture of humic and fulvic acids is received. Taking advantage of humic acids insolubility in acidic environment next allows to precipitate them by reducing reaction of the mixture. Many different extractants are used to obtain humic acids. Starting with the most aggressive like sodium hydroxide or potassium hydroxide, to more mild compounds among which sodium pyrophosphate and sodium tripolyphosphate are used. NaOH and KOH provide higher efficiency of extraction process, however they are suspected of simultaneous partial destruction of obtained compounds structure and contribution in contaminating product with other compounds [13, 14]. Less destructive are compounds like $Na_4P_2O_7$ or $Na_5P_3O_{10}$, but they guarantee higher purity of the product concurrently lowering the productivity [11, 15, 16]. Course of the extraction also depends on temperature of the process, time and additional factors, like speeding up the extraction with ultrasonic waves [2, 17, 18].

Many methods, patents and industrial standards concerning humic acids extraction from lignite strictly describe fineness of used raw material, which clearly suggest that it influences on course and efficiency of the process [3, 9]. Economic factors also determine the character of humic acids production on a mass scale. Therefore, it is essential to define optimum coal fineness, which provides the biggest profit after calculating extraction process efficiency and raw material grinding costs.

Materials and methods

The aim of research was to determine efficiency of humic acids extraction process, using different fineness of lignite. Lignite from Konin coal basin and Belchatow coal basin was analysed. Brown coal is an intermediate form between peat and hard coal, formed in neogen in Cenozoic. It is almost entirely used in power industry by burning in thermal power station next to the strip mine, because of its low rank of coal and high dampness. The alternative way of using this fuel, protecting the atmosphere from harmful chemical compounds emission, may be production of humic acids used next in agriculture.

Obtained this way humic acid in the form of gel, after desiccation and grinding down can be used separately as fertilizing agent or can be an additive to other fertilizers.

Factories in the United States and Germany already conduct this kind of production and in Poland fertilizing agents with humic acids addition are also available.

Four extractants were used in the research: sodium hydroxide, potassium hydroxide, sodium pyrophosphate and *sodium tripolyphosphate* (TPS), which were added to samples of four different fineness: 0.2 mm; 0.63 mm; 1.0 mm and 2.0 mm. After carrying out the extraction, carbon content was determined in direct extract including humic and fulvic acids and in pure humic acids. Carbon determination was made in accordance with modified Alten method.

Samples of given fineness were subjected to specific extractants: 0.1 M NaOH; 0.1 M KOH; 0.1 M $Na_4P_2O_7$; 0.1 M TPS in a proportion 1:20. Then mixtures were thoroughly blended, plugged with rubber stoppers, put into a shaker for 2 hours and left till next day. Obtained extracts were centrifuged and filtered to flasks from which there were taken samples for determination of organic carbon (C_{org}) in direct extract (HA + FA). The solutions which remained in flasks were subjected to 2 M H_2SO_4 and left for 24 hours in order to precipitate humic acids, which were filtered subsequently. After dissolving humic acids gel on filters using 2 % Na_2CO_3, samples of organic carbon in humic acids (HA) were taken for further analysis.

Carbon content in samples was determined in accordance with Alten method, which is based on oxidation of organic carbon with 0.34 M potassium dichromate(VI) in the presence of sulfuric acid during 3 hours heating in boiling water bath. Modification of this method is based on using Mohr salt and ferroin sulfate as an indicator for back titration of potassium dichromate(VI), while in the original method iodometry is used for this purpose.

Results and discussion

After analyzes and appropriate calculations following results were obtained (Table 1).

Based on these experiment results following conclusions may be drawn: For both lignite from Konin coal basin, and from Belchatow coal basin and independently of used extractant type, the efficiency of the process, expressed in organic carbon content in direct extract and humic acids, decreases as the fineness of raw material increases. Presumably, stronger fines size reduction provides growth of active surface subjected to extractant treatment and results in increase of humic acids extraction process efficiency. Direct extract has higher organic carbon content, because apart from humic acids it also includes fulvic acids, which are an additional source of organic carbon. The proportion between humic and fulvic acids amount is usually similar for each fineness of raw material and for both products analogous falling tendency is observable when fineness is growing. Furthermore, it is noticeable, that the most humic acids may be obtained when using sodium hydroxide for extraction, a bit less utilizing potassium hydroxide, whereas the least using sodium pyrophosphate or sodium tripolyphosphate. The effectiveness of the two last extractants is similar for each type of brown coal, at the same time it is worth stressing that for raw material from Konin coal basin sodium pyrophosphate turns out to be better, while lignite from Belchatow coal basin provides higher efficiency when using TPS for extraction. It is probably caused by the structure

Table 1

Organic carbon content in direct extract and humic acids obtained from lignite depending on fineness

Extractant type	Lignite fineness [mm]	C_{org} content in direct extract (HA+FA) [%]		C_{org} content in humic acids (HA) [%]	
		Konin	Belchatow	Konin	Belchatow
NaOH	0.2	56.2	45.4	41.9	19.2
	0.63	55.6	42.9	34.6	15.3
	1.0	48.5	37.2	32.0	14.5
	2.0	49.1	13.1	30.7	12.8
KOH	0.2	45.6	37.4	36.3	17.4
	0.63	41.0	36.6	27.3	14.5
	1.0	40.4	40.9	30.4	12.3
	2.0	39.7	26.4	19.4	12.2
$Na_4P_2O_7$	0.2	37.9	26.6	22.1	12.9
	0.63	36.5	15.9	17.9	12.3
	1.0	37.1	15.5	13.1	12.2
	2.0	37.2	9.4	15.5	8.0
TPS	0.2	31.5	28.8	19.3	14.2
	0.63	24.6	16.7	17.8	12.5
	1.0	26.2	15.7	13.2	12.0
	2.0	29.6	18.4	7.5	11.0

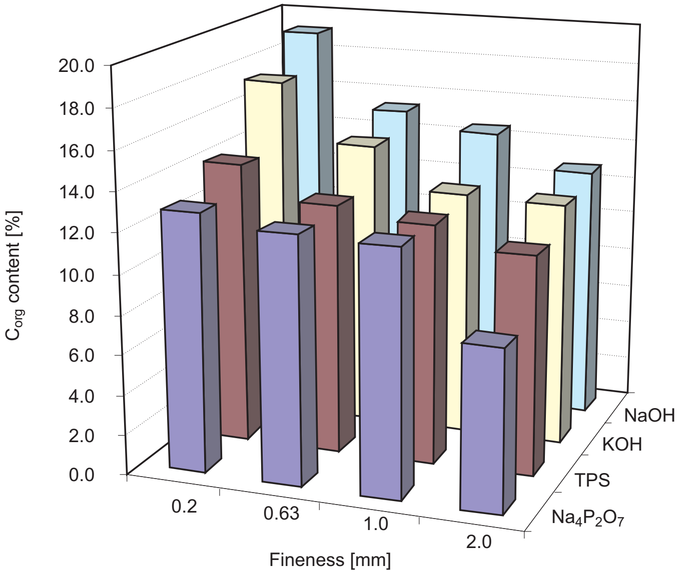

Fig. 1. Organic carbon content in humic acids obtained from lignite using different extractants

and composition of each lignite type and consequently different chemical affinity towards extractants. However, using hydroxides in this process, it is vital to remember about already mentioned destructiveness of NaOH and KOH, which may artificially inflate the efficiency of the process, due to additional impurities extracted form brown coal with the main product. The last thing worthy of attention is that lignite from Konin is richer in humic acids than coal from Belchatow.

Conclusions

The carried out researches proved that lower fineness of the raw material, lignite in this case, causes the increase of humic acids extraction process efficiency. The differences are more noticeable for brown coal from Konin, which shows that even 20 % increase in efficiency level is possible while reducing fines size from 0.63 mm to 0.2 mm. This tendency is probably connected with growth of active surface subjected to extractant treatment. Furthermore, the kind of chemical compound used in extraction is essential. Sodium hydroxide and potassium hydroxide provides higher efficiency of the process but at the cost of obtained humic acids quality. However, sodium pyrophosphate and TPS are less aggressive substances, so using them results in smaller amount of product, but purer and with better preserved structure. That is why it is important to define advisable quality of humic acids while choosing extractant. For instance, if the product is intended for using as a fertilizing agent mixed with other compounds, then it is reasonable to apply extractants obtaining a lot of humic acids, but partially impure, whereas using sodium pyrophosphate or TPS is recommended when high quality and purity of the product is required. Therefore, knowing raw material grinding costs, individual for each factory, and comparing them with the price of obtained product and its application, allows to estimate profitability of lignite grinding and find the best extractant type.

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OCENA WYDAJNOŚCI EKSTRAKCJI KWASÓW HUMINOWYCH Z WĘGLI BRUNATNYCH O RÓŻNYM UZIARNIENIU

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Abstrakt: Kwasy huminowe są grupą specyficznych związków organicznych, które powstają w skomplikowanych procesach biochemicznych, takich jak utlenianie, kondensacja oraz polimeryzacja wysokomolekularnych produktów rozkładu resztek pochodzenia roślinnego i zwierzęcego. Związki te ułatwiają przyswajanie mikroelementów przez rośliny, poprawiają strukturę gleby, wpływają korzystnie na jej porowatość, a tym samym napowietrzenie, retencję wodną oraz lepkość, zwięzłość i tworzenie struktur agregatowych gleb. Celem pracy było określenie wydajności ekstrakcji kwasów huminowych z różnych rodzajów węgla brunatnego, w zależności od jego uziarnienia. Większe rozdrobnienie surowca gwarantuje wzrost powierzchni aktywnej podlegającej działaniu ekstrahenta oraz zapewnia większą porowatość masy poddawanej ekstrakcji, zatem spodziewany jest wzrostu wydajności produkcji kwasu huminowego w miarę zmniejszania uziarnienia węgla brunatnego. Określenie optymalnego sortymentu, będącego kompromisem pomiędzy wydajnością ekstrakcji a kosztami rozdrobnienia surowca, pozwoli na ekonomiczną produkcję środka nawozowego, jakim jest kwas huminowy.

Słowa kluczowe: kwasy huminowe, wydajność procesu ekstrakcji, uziarnienie

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TECHNICAL PROBLEMS AND ECOLOGICAL RISKS IN CONNECTION WITH OPERATION OF COOLING WATER SYSTEMS

TECHNICZNE PROBLEMY I ZAGROŻENIA EKOLOGICZNE ZWIĄZANE Z EKSPLOATACJĄ SYSTEMÓW WODY CHŁODZĄCEJ

Abstract: Industrial water consumption in Poland is very high and reach over 10 billion m^3/year, which forces the implementation of appropriate programs and technological solutions to reduce water consumption in industrial activity. Depending on the design system, operating conditions of water-powered cooling systems, they are exposed to varying degrees of corrosion, precipitation and deposition of sediments and the growth of microorganisms in water circulating. So important are measures aimed at raising the technical level of operation of industrial water systems. One of the most promising ways to prevent negative phenomena in the operation of cooling water systems is the use of organic inhibitors of complex multi-functional system to protect against corrosion, deposition of sediments and the development of microorganisms in the water circulation.

Keywords: cooling water systems, corrosion, phosphonic compounds

A major problem in the operation of cooling systems, in which water is acting as the coolant, is the occurrence of adverse processes such as corrosion, precipitation and deposition of mineral sediments as well as microbial contamination of the environment and the formation of biological sediment.

Losses due to corrosion in Poland are estimated on 6–10 % of the gross domestic product. The 20–30 % of general corrosion losses and in the municipal economy even more than 40 % are losses associated with the operation of water systems [1].

In Poland, in many cooling water systems is still applied raw water, or untreated and non-inhibited water demonstrating the high corrosivity (carbon steel corrosion rate of 0.6–0.8 mm/year) and susceptibility to the formation of sediment. This is due to

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generally high-pass system, which leads to excessive water consumption [1–3]. Particularly important are efforts to reduce water consumption, because the fresh water resources in Poland are very small. In Europe, the average amount of water per capita is 4.560 m^3, while in Poland is three times smaller. In 2008 in Poland were used 10.234 billion m^3 of water, of which 7.504 billion m^3 are used for industrial purposes including chemical plants and 353.3 million m^3 [4]. Excessive consumption of water for industrial purposes can be reduced by reconstruction of the circular flow systems as well as by use of multi-inhibitors preparations. These activities would not only reduce water consumption, but also allow to apply effective system protection against corrosion, sludge formation and development of microorganisms even at high concentration of circulating water. The scale of the savings on water consumption in the operation of the cooling water circulation system can be assessed based on the make-up water demand and wastewater discharges to water, depending on the concentration ratio of circulating water (Table 1). The biggest savings in water consumption of 64–66 % is achieved by increasing the concentration of circulating water to 3.5–4.0. In a higher concentrating of water to 5.0–7.0 is achieved both a reduction in water consumption by 70–72 % and less water to reduce the discharges of wastewater but it greatly increases the risk of corrosion and deposition of sediments during the operation of systems [1].

Table 1

Demand up water desalination and size depending on the concentration ratio n (constant evaporation losses amount to100 m^3/hr) [1]

Concentration index [n]	Make-up water demand [m^3/hr[	Size of desludging [m^3/hr]
1.5	300	200
2.0	200	100
2.5	166	66
3.0	150	50
3.5	140	40
4.0	133	33
5.0	125	25
7.0	117	17

Proper exploitation of industrial cooling water circulating system plays an important role in raising the level of technical installations and increasing the competitiveness of many industries and products offered articles through national market on background of European market. However, it is also important that the technological solutions fulfill the conditions for sustainable development and particularly in the field of safe technologies and rational use of raw materials, energy and other materials, due to the protection and preservation of the environment. The methods of preparation and treatment using inhibitors will also let to use low quality water and wastewater from manufacturing processes for cooling purposes. Corrosion inhibitors may be introduced directly into the water to protect the circuit and all the installations, equipment and apparatus in contact with water, thus ensuring high economic effectiveness of the protection and maintenance of cooling systems [1, 3, 5–7].

Technical problems in the operation of cooling systems

Raw unfiltered water contains soluble and insoluble minerals, microbiological organisms, and dissolved gases in water that may cause during operation of the exploitation of cooling circulation reducing the efficiency of heat exchange. Due to its construction, open recirculating cooling systems are primarily exposed to the accumulation of pollutants by concentrating circulating water.

As a result of evaporation of water, pollution and present salts in water, undergo the accumulation in system, which may lead to intensification of adverse processes such as: corrosion, sediment formation and development of microorganisms. These processes are interdependent and have mutual influence on each other (Fig. 1). Corrosion processes and the accompanying adverse events occur in both closed and open cooling systems. However, due to a very complicated structure and operation of open recirculating systems dedicate them considerably larger attention [2, 5, 8–9].

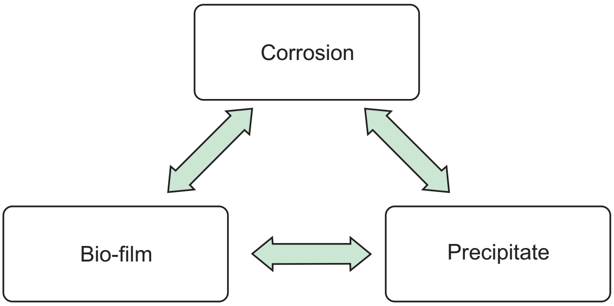

Fig. 1. The relation between the processes determining the state of cooling systems [8]

Proper operation of the water systems with recirculation require that such system has to remained ‘clean’, that is not formed any corrosion products and should not precipitated solids that favor the growth of microorganisms in the water circulation [1]. On the other hand, there is no clear requirement to be met by an open feed water cooling system. The current recommendations are usually determined based on experimental data developed by designers and engineers. Recommendations for water used regulate only a few key parameters, which include: general parameters, pH, hardness and salinity of the water. The individual limits specified parameters may vary among themselves to some extent, depending on construction materials used for the system [10].

Factors affecting the increase in water consumption during operation of the cooling system can be divided into two categories – physicochemical and biological. Physicochemical factors are responsible for such negative processes as precipitation of deposits on heated surfaces and corrosion of structural materials [11].

Corrosion processes of cooling systems are contingent on the type of construction materials, as well as the composition of the cooling water. Typical cooling systems are generally made of carbon steel, copper and brass. Cooling waters are contained in the Mercer's definition as inert corrosive environments. According to this definition, aquatic environments are neutral-phase systems, containing at least 50 % of the water about pH in range 5.5–10.0. Metal constructional materials in such solutions are covered with layers of durable natural oxide formed on the air. Under such conditions, these layers do not react with H^+ ions and OH^- to form soluble products. However, when in solution are present aggressive anions (Cl^-, SO_4^{2-}, HCO_3^-) layer can undergo electrochemical digestion. Neutral water environments are the most aggressive corrosive environments. Only in neutral aqueous environments may occur separately or simultaneously three types of corrosion cells (macro- and microcells, concentration cells, differential temperature cell) associated with electrochemical corrosion of metals [1, 12].

Electrochemical corrosion of metals is the dominant processes proceed in neutral aqueous environment, accompanied by an anodic oxidation reaction of metal. In the case of carbon steel (most often used constructional material) can be summarized as follows:

$$Fe \rightarrow Fe^{2+} + 2e$$

and the cathodic oxygen reduction reaction (when in solution are not present stronger oxidants). In aqueous environment at pH > 7 the reduction of oxygen proceeds according to the following reaction:

$$\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-.$$

Reactions of anodic metal oxidation and cathodic reduction of oxygen occur at the same rate, while the cathodic reaction is limited by diffusion of oxygen to the metal surface. Depending on the prevailing conditions, as a result of secondary reactions on the surface of the metal can be formed a layer constituting the barrier to the diffusion of oxygen. This layer consists of iron(II) hydrated oxide or iron(II) hydroxide. Dissolved oxygen is present in the water oxidizes the outer part of the layer of iron(III) hydrated oxide or iron(III) hydroxide

$$Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_3\downarrow \rightarrow Fe_2O_3 + 3H_2O.$$

There are cases where, because of unfavourable conditions, the oxide layer formation does not occur on metal surface but in volume of solution. The consequence of this is the formation of large quantities of precipitate that accumulate in such places where the flow rate is reduced. In such places also permanent water pollutions as well as biological deposits are accumulating [1].

The use of raw water as a coolant in open cooling systems in the industry is characterized by: high total hardness, alkalinity (balance carbonate), the presence of silicates and sulphates, which contribute to the formation of deposits in pipes, heat exchangers and other parts of installation. The formed sediments are the cause of development of underdeposit corrosion and increased action of microorganisms [13, 14]. In order to limit processes of the grow of deposits resulting from dominating interferences of the carbonate balance in the cooling system a stabilization of water is being conducted, which gives it such a property to ensure the storage and transmission of water without causing changes in the physical, chemical and biological agents. Various methods of the stabilization of water are being used for it without removing soluble salts, gasses and pollutants in stabilized water. Stabilization of water can be carried out by physical and chemical methods, or using a combination of both. Physical stabilization does not pollute the water and its scope includes: treating water in a magnetic, electromagnetic field, or by using ultrasonic waves. Methods of chemical stability of water rely on the introduction to the relevant chemicals. This creates a greater possibility of water treatment regardless of its composition (pH, salinity, dissolved gases) and the technical conditions of operation of the cooling system. The compounds for the chemical stabilization should among others create long-lasting but soluble complexes with ions Ca(II) and Mg(II), well dispersed organic sediments and should be safe for the environment [1, 3, 15]. Formation of complexes between the compounds and the stabilizing cations present in the water helps to reduce the concentration of these ions. The result is a lower rate of sediment deposition in the water.

The use of chemical stabilization can also reduce corrosion aggressiveness of water used in industrial cooling systems. A suitable method for the stabilization of water enables utilization for industrial purposes, poor quality of surface waters and wastewaters from manufacturing processes as a coolant in the working systems.

The presence of microorganisms (bacteria, fungi, algae) in circulating water is also undesirable from the corrosion point of view. Their presence is conditioned with the lack of microbiological stability of water and hydraulic conditions in the system. Microorganisms in the metabolic process breath (take oxygen) and produce metabolites--substances that can strongly stimulate the electrode processes, such as aggressive organic acids, sulphides [16]. Besides of this, microorganisms absorb the ingredients in the metabolism of the passive layer and corrosion-inhibiting substance particles. Cathode activity of microorganism manifests mainly by fabricating hydrogen ions by them. Local oxygen consumed in the process of respiration leads to the formation of the biofilm aeration alternating microcells, and the place of the oxygen-depleted surface are becoming privileged sites for the development of anaerobic bacteria. These bacteria in course of life processes produce metabolites such as H_2S, sulphides, polysulphides or thiosulphate, which are stimulators of corrosion of iron, especially in an environment containing hydrogen ions [17, 18]. Operation of the system in which microorganisms are present can lead to negative effects – from creating an insulating layer and inhibiting the flow of biofilm on heat transfer surfaces by microbial corrosion of structural materials. A common cause of accelerated corrosion of metals covered with a biofilm detachment of the biofilm clusters strongly associated with the original products of corrosion and surface display of open fragments exposed to aggressive environmental effects. Biological corrosion occurs more frequently at the impured than the pure metal, but the same kind of microorganisms for some metals may promote corrosion, and the other may lead to the inhibition [19].

Reduction of corrosivity of water in cooling systems

The protection of industrial water systems has the aim to reduce corrosion rate of construction materials, reducing the amount of mineral precipitate and accumulation it on the surface as well as to prevent microbial growth. Among many methods of protection against corrosion deserves a special attention the inhibitors protection, due to its simplicity, efficiency and versatility [3]. Research undertaken in the last 30 years concerning the application of corrosion inhibitors to protect the cooling systems have shown that the most effective are organic compounds containing phosphorus, which have multidirectional action. Organophosphorus compounds introduced into the system simultaneously provide corrosion inhibition, reducing the amount of deposits set aside, and their dispersion [20, 21]. Obtained desirable results are well show in the literature [3]. In one of the Polish Institutions of Nitrogenous Industry was used multifunctional blend inhibitor VFZ (the main component was trimethylophosphonic acid N-[$N(CH_2PO_3H_2)_3$]) for protection the cooling system with a capacity of 18000 m^3. This system was supplied with decarbonized water**.** During operation of the system followed by absorption of ammonia and reduction water pH 5.6–6.0. Circulation water was periodically contaminated by ions Cu(II), which increased the risk of corrosion and sediment formation. The corrosion rate of carbon steel and copper operation in such conditions was, respectively: 0.71–0.89 mm/year and 0.05–0.27 mm/year. The rate of sediment deposition was 11.47–12.38 g/(m^2day). Introduction of corrosion protection by VFZ inhibitor reduced the corrosion rate of both carbon steel 0.12 mm/year and the corrosion rate of copper to 0.013 mm/year. It was also limiting the rate of precipitation to 0.95 g/($m^2 \cdot$ day). Application of this inhibitor caused a reduction in consumption of decarbonized water to supply the 1.100 thousand m^3 (before safe annual water consumption was 2.424 thousand m^3 and after the introduction of inhibitor – 1315 thousand m^3). Therefore it has limited scope and frequency of repairing works about 50 %.

The use of multifunctional inhibitor reduces water consumption for industrial purpose, reduces the corrosiveness of water and the introduction of unnecessary chemicals to enhance the effectiveness of the protection of the cooling system.

Despite the many advantages of corrosion inhibition these compounds have also disadvantages. These compounds are characterized by too much phosphorus in its molecule. Phosphorus found in the water contributes to growth of phytoplankton, resulting the formation of so-called algal bloom on its surface. From 1 January 2000 applicable regulation introduced in 1991 by the Minister of Environment and Natural Resources and Forestry, which establishes the reduction of total phosphorus in the wastewater entering the flowing waters and see waters from the amount of 5 mg/dm^3 to 1.5 mg/dm^3 [21]. Therefore, the research began looking for new organophosphorus compounds, with smaller quantities of the phosphonic groups, but with the same good inhibition properties.

Conclusion

Long-term, failure-free work of cooling system, while maintaining its full capacity, is associated with the provision of adequate water treatment. This requires taking into consideration process of processing of water treatment and circulation [10, 11]. A build-up of adverse phenomena will be a consequence of wrong preparing water and the bad exploitation of the cooling system. They may be the result of frequent breakdowns, renovation breaks, the use of oversized equipment, increased water consumption, energy losses due to additional resistance to water flow because of the layers of sediment formed.

Effective and yet economical solution is to use multifunctional organophosphorus inhibitors. However, due to increasingly restrictive regulations regarding protection of natural environment led to research on finding new compounds. They should be characterized by: high corrosion performance and anti-scaling performance at low concentrations, non-toxicity, stability and duration of action as well as availability of raw materials for their manufacture. One of the promising possibilities for the production of these compounds is the use of waste materials from industry. This will also help to reduce the amount of generated wastes, which will positively affect the environment.

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TECHNICZNE PROBLEMY I ZAGROŻENIA EKOLOGICZNE ZWIĄZANE Z EKSPLOATACJĄ UKŁADÓW WODY CHŁODZĄCEJ

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Abstrakt: Zużycie wody przemysłowej w Polsce jest bardzo duże i wynosi ponad 10 mld m^3/rok, co zmusza do wdrażania odpowiednich programów i rozwiązań technologicznych w celu zmniejszenia zapotrzebowania na wodę. W zależności od rozwiązań konstrukcyjnych, warunków eksploatacji układów chłodzących zasilanych wodą, narażone są one w różnym stopniu na korozję, wytrącanie i odkładanie się osadów oraz rozwój mikroorganizmów w wodzie obiegowej. Dlatego ważne są działania mające na celu podnoszenie poziomu technicznego eksploatacji przemysłowych układów wodnych. Jednym z najbardziej perspektywicznym sposobem zapobiegania negatywnych zjawisk występujących przy eksploatacji układów wody chłodzącej jest stosowanie ekologicznych wielofunkcyjnych inhibitorów kompleksowo chroniących układ przed korozją, odkładaniu się osadów i rozwojem mikroorganizmów w wodzie cyrkulacyjnej.

Słowa kluczowe: układy wody chłodzącej, korozja, związki fosfonowe

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ADSORPTION NAPHTOL GREEN B ON ACTIVATED CARBON F-300

ADSORPCJA ZIELENI NAFTOLOWEJ B NA WĘGLU AKTYWNYM F-300

Abstract: In the present study, the sorptive capacity of activated carbon F-300 in the removal of dyes from textile wastewaters, was estimated. Dye – naphtol green B – were chosen to study, and as adsorbent we have chosen the activated carbon F-300, virgin and regenerated. Fenton reagent, which is good oxidant, was used for activated carbon regeneration. The iodine number, which was measured according to the directive PN-83 C-97555.04, was used to evaluate sorptive capacity of regenerated activated carbon. Dye concentration was 400 mg/dm^3. Sorption abilities of activated carbon were expressed by mass balance relationship in case of fresh activated carbon it was 21 mg/g, and after regeneration – from 22 mg/g to 33 mg/g. The highest removal efficiency was 88 % (carbon after 4th regeneration), the lowest – 74 % for virgin carbon. The experimental data adsorption isotherms were defined. Adsorption theoretical models Freundlich or Langmuir were selected. The value of the correlation coefficient (r^2) showed better fit to Langmuir model. The experimental data shows that chosen activated carbon can be used for the decontamination of dyes from textile wastewater. However, model tests need to be verified on real wastewater samples.

Keywords: dye adsorption, activated carbon, Fenton reagent, naphtol green B

1. Introduction

Dyes are natural or synthetic colorants used in various industries such as textiles, tanneries, paints, pulp and paper [1]. Synthetic dyes are indispensable to the textile and dyeing industries. The use of dyes, as most chemicals, can be hazardous [2]. Physical and chemical properties of dyes make them sparingly biodegradable, toxic, carcinogenic and mutagenic compounds [3]. Dyes are classified on a few groups such as acid dyes, basic dyes, disperse dyes, direct dyes, reactive dyes, solvent dyes, sulphur dyes, vat dyes and others [4]. The colour of dyes is provided by the presence of a chromophore groups. A chromophore is a radical configuration consisting of conjugated double bonds containing delocalised electrons. The chromogen, which is the aromatic structure usually containing benzene, naphthalene or anthracene rings, is part of chromogen – chromo-

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phore structure along with an auxochrome. Common chromophore groups are azo (-N=N-), nitroso (-NO or N-OH), nitro (-NO_2 or =NO-OH), sulfur (C=S) and others [5].

The removal of contaminants from the effluents is problematic with established technologies often unable to adequately reduce contaminant concentrations. This has initiated a search for more effective, economic treatment techniques, of which adsorption processes appear to offer significant potential. The conventional wastewater treatment such as biological treatment process is not very effective in treating a dyes wastewater. It is also treated by physical or chemical processes, but these processes are very costly and cannot effectively be used to treat the wide range of compounds [6]. Methods used to treat wastewater containing dye include coagulation-flocculation [7], advanced oxidation process [8], adsorption[9] and membrane technology [10]. The adsorption process is one of the effective methods for removal dyes from the textile wastewater [6].

Adsorption is a flexible process that may be fully automated, incur significantly lower capital costs than, for example, ozone, membrane or biological processes [11].

Activated carbons are mainly used to remove organic and inorganic compounds from the water [12–13]. The various kinds of activated carbons are used in Polish waterworks such as granulated activated carbon, for example WD-extra, WG-12, or granular one PICA, F-300 [14]. The sorptive capacity of activated carbon depend on the properties of pores, *ie* their surface area and size, chemical nature of the surface, structure and chemical properties of dissolved organic substances and other substances, which can be absorbed by activated carbon [15].

Activated carbons can be regenerated during a various processes such as thermal and chemical methods [16]. Oxidation of organic chemical pollutants by Fenton reagent with hydroxyl radical OH is one of chemical regeneration methods [17]. The Fenton reagent is defined as a mixture of hydrogen peroxide and iron(II) ion ($H_2O_2 + Fe^{2+}$) and it is effective for color and COD removal of dye effluent [18–19]. The one of the regeneration's advantage is fact that it is cheaper than changing the deposit on new one.

According to the previous works [20–23] concerned possibility of sorption of dyes on activated carbon, the present work deals with checking sportive capacity of virgin and regenerated by Fenton reagent activated carbon F-300 with reference to dye – napthol green B.

2. The material and methods of investigations

2.1. Activated carbon characteristics

Activated carbon called F-300 is used for removal of organic pollutants (detergents, petrochemicals, grease, amines, oils) from municipal or industrial (production of bearings) wastewaters. Exhausted activated carbon was regenerated by Fenton reagent.

2.2. Dye characteristics

Napthol green B (Acid green 1) belongs to nitroso group dyes (Fig. 1). This dye is very well soluble in water and its molar mass is 878.79 g/mol. Industrial napthol green

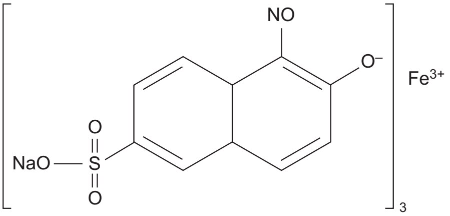

Fig. 1. Naphthol green B

B is a product which contain 50 % of clean dye. Dye as an anion is ranked as acidic dyes [24]. Naphthol green B is used to dye cotton, nylon and paper. It can be found in textile and printing wastewater.

2.3. Course of the experiment

2.3.1. Adsorption on virgin activated carbon

Virgin F-300 activated carbon (0.2 g, 0.5 g, 1 g, 1.5 g, 2 g, respectively) was placed in conical flasks (300 cm^3). Then 100 cm^3 volumes of the solution of napthol green B, having the concentration of 400 mg/dm^3, were added to the flasks and the contents were shaken for ten hours. After that time, the phases, *ie* the dye solution and the spent sorbent, were separated. F-300 activated carbon was then washed with distilled water and dried in a dryer.

2.3.2. Adsorption on regenerated activated carbon

Following adsorption, F-300 activated carbon was regenerated using Fenton reagent. The latter was prepared in the following way: distilled water was poured into 1 dm^3 beaker, then concentrated sulphuric(VI) acid was added, in such a way so that pH ranged around 3. To so prepared solution, 10 cm^3 of $FeSO_4 \cdot 7\ H_2O$ (the amount of ferrum ions 9.27 mg) and 1.5 cm^3 of hydrogen peroxide were added. WDex activated carbon was treated with Fenton reagent solution (500 cm^3) prepared in a way described above, then it was stirred for 15 min. Activated carbon was then washed with distilled water, afterwards the regeneration process was repeated. Thus regenerated F-300 activated carbon was used again to adsorb dyes mixture on it.

2.3.3. Determination of dye concentration

Spectrophotometric method was used to determine the concentration of dyes. Marcel Media UV/VIS Spectrophotometer was employed. First, spectra of naphthol green B were recorded and it has the $\lambda = 715$ nm wavelength maximum. Following the sorption process, samples of dyes were taken from a conical flask using a pipette and placed into a plastic cell and then they were put into the spectrophotometer. The concentration of dye was read on the computer and measured at determined concentration.

2.3.4. Changes in carbon parameters during the experiment

The process of adsorption and regeneration of activated carbon was also evaluated during an experiment. It was noted that regeneration process was significantly limited due to a loss of carbon mass. The mass of the virgin activated carbon has decreased from 15.000 g to 10.021 g (Table 1).

Table 1

Changes in carbon parameters during the experiment

Sorbent type	Mass	Mass loss [%]
Virgin carbon	15.000	
Carbon after the first regeneration	13.742	8.39
Carbon after the second regeneration	12.485	16.77
Carbon after the third regeneration	11.801	21.33
Carbon after the fourth regeneration	11.167	25.55
Carbon after the fifth regeneration	10.698	28.68
Carbon after the sixth regeneration	10.021	33.19

The sorptive capacity of regenerated carbon was measured by changes of iodine number (Table 2), which was evaluated according to directive no. PN-83 C-97555.04. Iodine number was the highest after the 1st regeneration, and it was the lowest for virgin carbon F-300.

Table 2

Iodine number

Activated carbon	Iodine number
Virgin carbon	507.68
After the first regeneration	666.33
After the second regeneration	656.811
After the third regeneration	634.6
After the fourth regeneration	647.119
After the fifth regeneration	644.119
After the sixth regeneration	644.119

3. Results and discussion

At the first stage of investigations surface sorption was calculated from following formula [25]:

$$A = \frac{(C_0 - C_i) \cdot V}{m_c},$$

where: C_0 and C_i – dye initial and equilibrium concentration, respectively;
V – solution volume,
m_c – mass of dry activated carbon.

On the basis of calculated values of surface sorption, it was possible to plot sorption isotherms (Fig. 2).

The highest surface sorption on virgin carbon for naphthol green B was 21 mg/g. As regards regenerated carbon, it ranged from 22 mg/g to 32 mg/g. Experimental data indicate that F-300 activated carbon has good sorptive properties according to

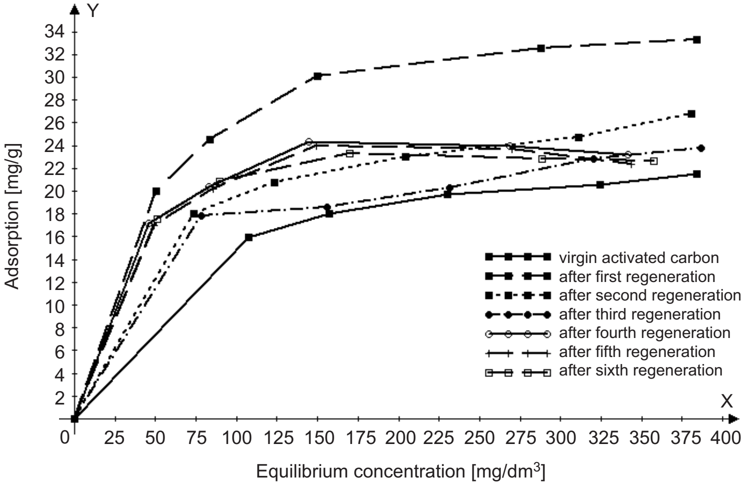

Fig. 2. The isotherms of naphthol green B on virgin and regenerated active carbon F-300

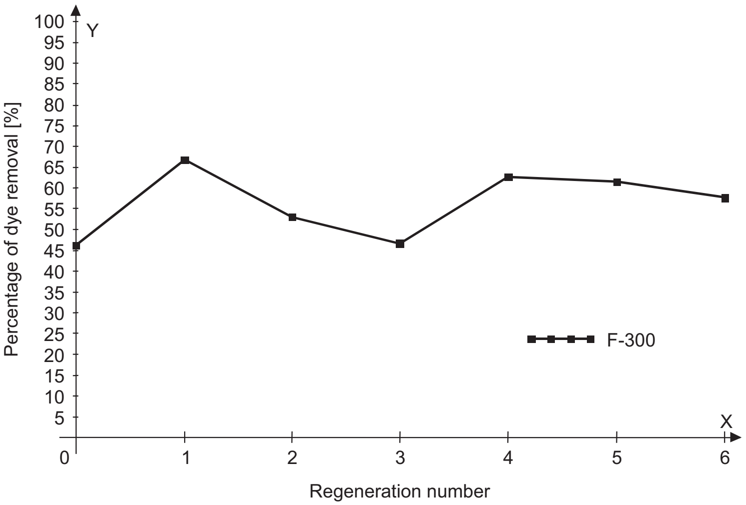

Fig. 3. Percentage of naphtol green B removal for virgin and regenerated activated carbon for $m_c = 1$ g

experimental models. Regeneration with Fenton reagent, however, slightly improves sorptive properties of activated carbon.

The experimental data allowed to evaluate dependence of selected dye removal percentage on subsequent regeneration cycles (Fig. 3). The percentage removal of virgin activated carbon F-300 was 46 % (carbon mass equal 1 g). As regards regenerated carbon (carbon mass equal 1 g), the percentage of removal ranged from 46 % to 66 %.

At the next stage of investigations, an attempt was made to fit an adsorption model to experimentally obtained isotherms. Two models, *ie* Freundlich equation and Langmuir equation, were used to analyse adsorption isotherms.

The Langmuir equation [26], applied to determine adsorption results, is based on the assumption that the adsorption maximum corresponds to the sorbent surface being saturated with adsorbed molecules of constant energy, and additionally, no migration of adsorbed substance on the sorbent plane takes place. The Langmuir equation can be presented in the following form:

$$\frac{C}{A} = \frac{1}{a_m \cdot k} + \frac{1}{a_m} \cdot C$$

where: C – dye concentration in the solution,
A – adsorption,
k – a constant related to adsorption heat,
a_m – adsorbed surface.

The Freundlich isotherm [27] is the earliest developed relation that expressed sorption equation. The Freundlich model follows the formula:

$$A = k \cdot c^{1/n}$$

where: a – adsorption,
C – concentration,
k – the Freundlich constant,
$1/n$ – the Freundlich exponent,

or in the logarithmic form:

$$\log a = \log k + \frac{1}{n} \log C$$

It should be noted that the higher is the value of the correlation coefficient (r^2), the better is the fit of the theoretical model to the experimental isotherm.

On the basis of calculated correlation coefficients (Table 3), it can be stated that for naphtol green B adsorption on virgin and regenerated carbon F-300, the Langmuir model better describes experimental results.

An exemplary Freundlich isotherm for activated carbon F-300 after the second regeneration for naphthol green B is shown in Fig. 4 and an exemplary Langmuir isotherm after the sixth regeneration is presented in Fig. 5.

Table 3

Parameters of Freundlich and Langmuir isotherms

Activated carbon	Freundlich isotherm			Langmuir isotherm		
	k	r^2	n	k	r^2	a_m
Virgin	5.69	0.979	4.464	0.044	0.988	22.222
After the first regeneration	8.016	0.93	4.048	0.044	0.991	34.483
After the second regeneration	6.807	0.99	4.386	0.039	0.985	27.027
After the third regeneration	7.603	0.899	5.347	0.041	0.983	24.39
After the fourth regeneration	10.069	0.755	6.452	0.122	0.996	24.39
After the fifth regeneration	10.162	0.697	6.711	0.147	0.994	23.256
After the sixth regeneration	11.376	0.763	8.000	0.146	0.0998	23.256

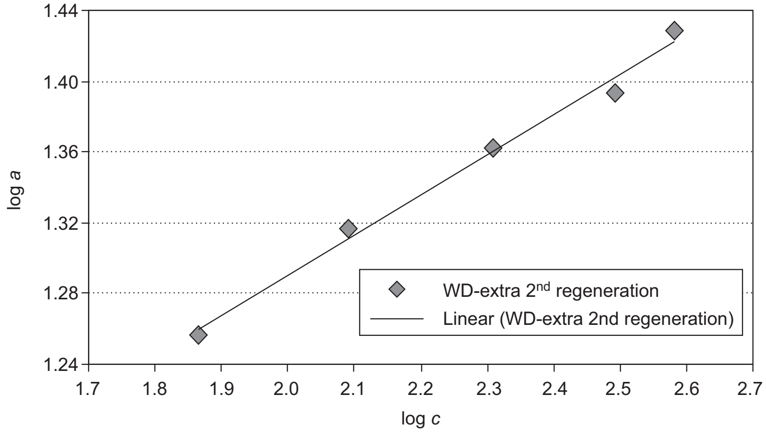

Fig. 4. Freundlich isotherm for F-300 activated carbon after the 2nd regeneration – naphthol green B

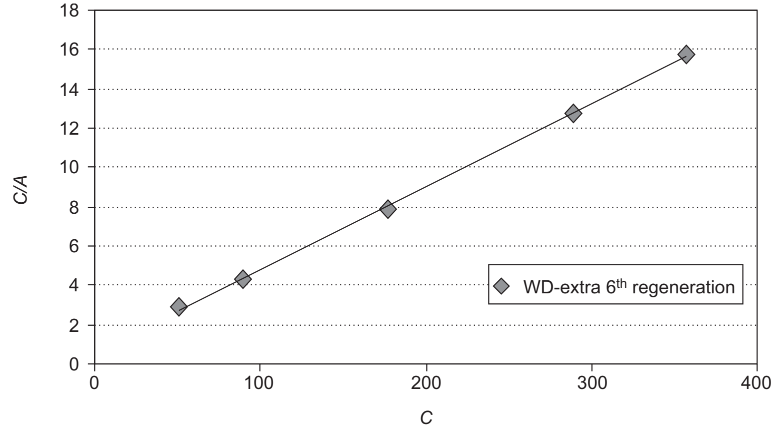

Fig. 5. Langmuir isotherm for F-300 activated carbon after the 6th regeneration – naphthol green B

4. Conclusions

The most important task of experiment was to check sorptive capacity of virgin and regenerated granular activated carbon F-300.

Summing up model investigations into selected dye described above it can be stated that:

– F-300 activated carbon demonstrates high sorptive capacity, which is confirmed by experimental results,

– Fenton reagent used for regeneration made it possible to maintain carbon sorptive capacity,

– a disadvantageous phenomenon that accompanies sorption on regenerated carbon is a sorbent mass loss,

– iodine number confirms better sorptive capacity for regenerated activated carbon than for virgin one,

– the Langmuir model better describes experimental results.

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ADSORPCJA ZIELENI NAFTOLOWEJ B NA WĘGLU AKTYWNYM F-300

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Abstrakt: W pracy podjęto próbę oceny możliwości użycia węgla aktywnego F-300 do usuwania barwników ze ścieków farbiarskich. Do badań wybrano barwnik – zieleń naftolową B, a jako sorbent zastosowano węgiel aktywny F-300 świeży i regenerowany. Regeneracja została przeprowadzona za pomocą odczynnika Fentona, który jest doskonałym utleniaczem. Zdolności sorpcyjne węgla po regeneracji oceniano poprzez zmiany wartości liczby jodowej, która została wyznaczona zgodnie z normą PN-83 C-97555.04. Stężenie barwnika wynosiło 400 mg/dm^3. Zdolności sorpcyjne węgla świeżego wyrażone wartością adsorpcji właściwej, która wynosiła 21 mg/g, a po regeneracji – od 22 mg/g do 33 mg/g. Na postawie danych eksperymentalnych wykreślono izotermy sorpcji. Najwyższy stopień usunięcia zieleni naftolowej B z roztworu wodnego wyniósł 88 % (po IV regeneracji), a najniższy – 74 % (węgiel świeży). Dopasowano teoretyczny model adsorpcji, tj. model Freundlicha lub Langmuira. Wartość współczynnika korelacji wskazuje na lepsze dopasowanie modelu Langmuira. Otrzymane wyniki wskazują, iż wybrany sorbent zarówno w postaci świeżej, jak i zregenerowanej może być stosowany w procesach usuwania barwników ze ścieków farbiarskich. Jednak badania modelowe muszą zostać sprawdzone na realnych próbkach ścieków.

Słowa kluczowe: adsorpcja barwników, węgiel aktywny, odczynnik Fentona, zieleń naftolowa B

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HERBICIDE TOXICITY TO THE CALIFORNIA EARTHWORMS *Eisenia fetida* Sav. and *Dendrobaena veneta* Rosa

WPŁYW TOKSYCZNOŚCI HERBICYDÓW NA DŻDŻOWNICE KALIFORNIJSKIE *Eisenia fetida* Sav. i *Dendrobaena veneta* Rosa

Abstract: This paper aims at estimating influence of selected herbicides on earthworms *Eisenia fetida* and *Dendrobaena veneta* survival abilities in toxic environment and on their reproduction cycle. Parameters taken into account:

- changes in fatality rate after applying toxins compared with the control,
- number of laid cocoons and hatchings,
- lethal concentration (LC_{50}).

Herbicides containing the following active substances: urea, aminophosphonic and phenoxyacid were chosen, as chemical material.

Earthworm responded differently to every herbicide. Significant decrease in body weight under the influence of linuron and decrease of the hatching rate under the influence of gliphosate and phenoxyacids.

Keywords: herbicides, *Lumbricidae,* life activity, reproduction

Earthworms (*Lubricidae*) being an important part of soil mesofauna decide upon biological activity of the soil and indirectly – upon its fertility. They are specifically adapted to variable habitat and life conditions [1–3].

Earthworms' activity creates favourable life conditions for many soil animals and for plants. *Lubricidae* are also an excellent source of information on environmental pollution due to their easy culture and broad range of occurrence. Because of these reasons, earthworms are considered indicator animals and are used in field and laboratory tests. Application of plant protection chemicals is not harmless to natural environment affecting eg the life cycle of oligochaetes. The effect might be direct or

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indirect. Pesticides, including herbicides, may affect earthworms directly causing their death or indirectly by changing their reproduction and/or behaviour. Moreover, herbicides *via* earthworms may enter higher links of the trophic chain [4–6].

Almost all herbicides are phytotoxic also for plants they have to protect. They show lower acute toxicity as compared with other plant protection means. Circa 13 % of herbicides is included in the I or II class of toxicity [7].

Material and methods

Two species of the California earthworms *E. fetida* and *D. veneta* kept in universal soil were used in experiments. They were taken from the own culture of the Department of Zoology, Warsaw University of Life Sciences. Adult individuals were used in tests which lasted circa 50 days for each experimental variant. The following herbicides were applied: Bofix 260EC, Afalon 450SC and Glifocyd 360 SL (Table 1).

Table 1

Characteristics of plant protection chemicals

Herbicide	Common name	Chemical name	Chemical group	Chemical formula
Afalon 450 SC	linuron	3-(3,4-dichlorophenyl)-1-methoxy-1--methylurea	derivative of urea	$C_9H_{10}Cl_2N_2O_2$
Bofix 260 EC	fluoroxypyr	((4-amino-3,5-dichloro-6-fluoro-2--pyridinyl)oxy)acetic acid,	derivative of pyridinocarboxylic acid (phenoxy acids)	$C_7H_5Cl_2N_2O_3$
	chlopyralid	3,6-dichloropyridine-2-carboxylic acid,	derivative of carboxylic acid	$C_6H_3Cl_2NO_2$
	MCPA	4-chloro-*o*-tolyloxyacetic acid	derivative of phenoxy acids	$C_9H_9ClO_3$
Glifocyd 360 SL	gliphosate	*N*-(phosphonomethyl)glycine	aminophosphoniates	$C_3H_8NO_5P$

Concentrations applied in experiments were 2–3 times lower than those recommended by the producers. Afalon and Bofix were used in concentration of 2.5 cm^3 per 600 cm^3 of water and Glifocyd – in concentration of 5 cm^3 per 600 cm^3 of water. The effect of the active substances of the herbicides was observed for 24 and 48 hours. Earthworms were not fed during that time. The control group consisted of earthworms kept in boxes to which distilled water was added. Experiments were carried out at a temperature of 25–28 ^oC.

After 48 hours the earthworms were left alone until the appearance of cocoons which were collected and transferred to other containers. Each experiment was triplicated with the use of 20 mature individuals per sample. To estimate mean *lethal concentration* (LC_{50}) for earthworms the containers were filled with 200 cm^3 of scalded and dried soil and poured with 50 cm^3 of herbicide solutions. Observations were carried out for 2 days.

Results and discussion

Limited mobility and migration at short distances made earthworms the appropriate organisms for monitoring chemical pollutants [8, 9]. *E. fetida* due to high genetic homogeneity and reproduction became a model species in tests for the harmfulness of chemical substances to saprophagous invertebrates [10]. When monitoring environmental pollution with earthworms one should consider their ability to accumulate heavy metals and other components of plant protection chemicals.

The decrease of bioconcentration and bioaccumulation of pesticide is a result of reduced absorption caused by metabolic processes of soil organisms and by defence mechanisms of earthworms such as the release of larger amounts of slime [11, 12]. In performed experiments Glifocyd 360 SL caused such a reaction in both earthworm species. The defence mechanism in *D. veneta* lasted during the whole experiment, which consequently affected the number of laid cocoons (Table 2). The response to herbicides involved also the irritation or burn of dermatitis and muscular sack and increased sensitivity of the nervous system. These results confirm observations done by Kamionek et al (2005) [13]. Irritation of the nervous system was observed in both species 48 hours after exposition. Later, non-coordinated movements and hypersensitivity to light were observed in the case of Bofix 260 EC. In the case of Glifocyd application the symptoms subsided after 10 days. Earthworms are also characterised by remarkable ability to adapt to changing environmental conditions. However, herbicides caused increased mortality short after their application [5, 13].

Table 2

The effect of herbicides on the California earthworms

Herbicide	Reaction to active substance of herbicide		Number of cocoons		Number of young individuals	
	E. fetida	*D. veneta*	*E. fetida*	*D. veneta*	*E. fetida*	*D. veneta*
Control	n.c.	n.c.	634	664	668*	572*
Afalon 450 SC	losses of coelomatic fluid, death, convulsions and non-coordinated movements, micro--wounds	losses of coelomatic fluid, death, convulsions and non-coordinated movements	1	2	0	0
Bofix 260 EC	sensitivity to the touch, death and escapes	sensitivity to the touch, death and escapes	201	383*	292	468
Glifocyd 360 SL	loss of body firmness, slowed movements, infrequent death	loss of firmness or “bloat” of the body, overproduction of slime, slowed movements	458*	206	627	234*

* Correlation significant at $p < 0.01$ (two-sided).

High earthworm mortality was observed after application of Afalon 450 which was finally reflected in their reproductive abilities. The least toxic appeared glyphosate containing Glifocyd 360 SL which reduced the population by circa 18 %. Mosleh et al

[11] demonstrated that isopoturon accumulated in the earthworms' bodies did not necessarily cause their death. Active substances and their metabolites may, however, exert sublethal effects like eg growth inhibition [11, 14]. In performed experiment such response was observed for Bofix 250 EC and Glifocyd 360 SL. The strongest reaction was observed in Glifocyd treated young individuals of *E. fetida* and *D. veneta* which reached the size of 1 cm and matured (Photo 1) lying deformed cocoons (Photo 2).

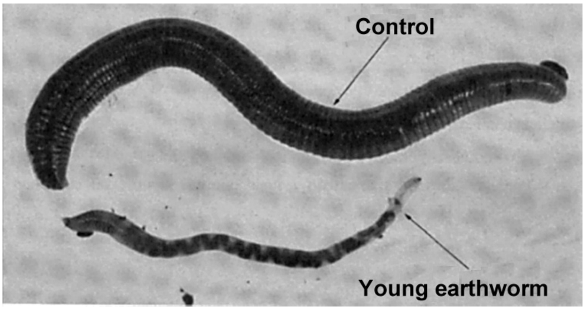

Photo 1. Young individual of *D. veneta* after the contact with herbicide compared with the control one

Photo 2. Deformed cocoons of *E. fetida* after the contact with Glifocyd

Experimentally measured mean lethal concentration (LC_{50}) of Bofix 260 EC was 4.17 mg/dm^3 for both species being lower than the dose recommended by the producer. The lethal concentrations of Glifocyd 360 SL were many times higher and amounted to 160 and 320 mg/dm^3 for *D. veneta* and *E. fetida*, respectively.

Conclusions

1. Applied herbicides caused irritation of the nervous system and of dermatitis and muscular sack dermatitis in *E. fetida* and *D. veneta*.
2. Herbicides containing linuron and glyphosate as active substances inhibited the growth of earthworms and development of young individuals after hatching.

3. All applied herbicides negatively affected reproduction of analysed oligochaete species.

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WPŁYW TOKSYCZNOŚCI HERBICYDÓW NA DŻDŻOWNICE KALIFORNIJSKIE
Eisenia fetida Sav. i *Dendrobaena veneta* Rosa

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Szkoła Główna Gospodarstwa Wiejskiego w Warszawie

Abstrakt: Celem przeprowadzonych badań było określenie toksycznego wpływu wybranych środków ochrony roślin na dżdżownice *E. fetida i D. veneta* na ich zdolność do przeżywania w środowisku oraz reprodukcję. Pod uwagę wzięto takie parametry, jak:

– zmiany w liczebności po zastosowaniu środka chemicznego w porównaniu z kontrolą,
– liczba składanych kokonów i wylęg,
– średnie stężenie śmiertelne (LC_{50}).

Jako materiał chemiczny wybrano herbicydy zawierające substancje czynne z grupy: mocznikowej, aminofosfonianowej i fenoksykwasów. Reakcja dżdżownic na zastosowane herbicydu była różna. Zaobserwowano znaczne zmniejszenie masy ciała pod wpływem linuronu oraz spadek liczby wylęgających się osobników pod wpływem glifosatu i związków z grupy fenoksykwasów.

Słowa kluczowe: herbicydy, *Lumbricidae*, reprodukcja, aktywność życiowa

Varia

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