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Elena MASAROVIČOVÁ[1] and Katarína KRÁĽOVÁ[1]

OCCURRENCE, CHARACTERIZATION AND ACTION OF METAL NANOPARTICLES

WYSTĘPOWANIE, CHARAKTERYSTYKA I DZIAŁANIE NANOCZĄSTEK METALI

Abstract: Metal nanoparticles (MNPs) are attracting attention for many technological applications as catalysts, in optical materials, medical treatments, sensors, and in energy storage and transmission. The function and use of these materials depend on their composition and structure. A practical route for synthesis of MNPs is by chemical procedure and by use of biological material ("green synthesis" as a dependable, environmentally benign process) including bacteria, algae and vascular plants (mainly metallophytes). Currently, there are various chemical and physical synthetic methods used for preparation of metal nanoparticles and several experimental techniques aimed at controlling the size and shape of MNPs. Toxic effects of MNPs on plants could be connected with chemical toxicity based on their chemical composition (*eg* release of toxic metal ions) and with stress or stimuli caused by the surface, size and shape of the particle. The physicochemical properties of nanoparticles determine their interaction with living organisms. In general, plant cells possess cell walls that constitute a primary site for interaction and a barrier for the entrance of nanoparticles. Inside cells, nanoparticles might directly provoke either alterations of membranes and other cell structures or activity of protective mechanisms. Indirect effects of MNP depend on their chemical and physical properties and may include physical restraints, solubilization of toxic nanoparticle compounds, or production of reactive oxygen species. However, it should be stressed that impact of MNPs on human and environmental health remains still unclear. Thus, evaluation scheme for national nanotechnology policies (that would be used to review the whole national nanotechnology plan) was recommended. The three following criteria for policy evaluation were suggested: appropriateness, efficiency and effectiveness.

Keywords: behaviour, direct and indirect effects, green synthesis, living organisms, metal nanoparticles, plants

Introduction

During the past two decades the nanotechnology field (including nanoparticles) has attracted overwhelming interest not only the scientific community but from business and political representatives, too. Such great attention is connected at least with three reasons. First of all, the nanotechnology achievements and their realization lead to the radical changes in all fields of human activity such as traditional and advanced technique, electronics and information technology, power and chemical engineering, agriculture and environment, medicine and biotechnology, human health and security, defence and transport, etc. Secondly, it is turned out that nanotechnologies really had created many interdisciplinary research directions, where now many specialists of the wide diversity are concentrated. At present, nanotechnology is associated not only with traditional natural sciences (such are physics, chemistry, biology, materials science) but also with lot of technologies and many social and economic sciences. Third reason it is, that this topic has revealed many gaps in fundamental natural-science knowledge, in technology as well as in social sciences (in detail see [1]).

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In general, *nanoparticles* (NPs) - as the main component of nanotechnology - are atomic or molecular aggregates with dimension between 1 and 100 nm that can drastically modify their physico-chemical properties compared with the bulk material. NPs can be made from variety of bulk materials and they can act depending on chemical composition, size or shape of the particles. There were identified three types of NPs: natural, incidental and engineered. The first one has existed from the beginning of the earth´ history and still occurs in the environment (*eg* volcanic or lunar dust, mineral composites). Incidental (waste or anthropogenic) NPs are results of industrial processes (*eg* diesel exhaust, coal combustion, welding fumes) [2]. The last type of NPs can be divided into the following four groups: (1) carbon based materials - single or multiwalled carbon nanotubes; (2) metal based materials - quantum dots, nanogold, nanozinc, nanoaluminium, TiO_2, ZnO and Al_2O_3; (3) nano-sized polymers built from branched units with specific chemical functions; (4) composites nanoparticles which combine nanoparticles with other nanoparticles or with larger bulk-type materials [3]. There is now an extensive discussion about the risks of the anthropogenic or engineered NPs into environment, plants as well as human health. The authors [4] summarized information concerning the current status, knowledge gaps, challenges and future needs of NPs ecotoxicology. These authors concluded that NPs can be toxic to bacteria, algae, invertebrates and fish species, as well as to mammals.

Since the early 1990s, enormous efforts worldwide have led to the production of many types of nanomaterials. The interest in nanomaterials is a result of extreme dependence of properties, mainly electronic, magnetic, optical, and mechanical. In the field of nanotechnology, the controlled synthesis of NPs size, shape and monodisperdity is essential in order to explore their unique chemical and physical properties. Currently, there are various chemical and physical synthetic methods used for preparation of nanoparticles and several experimental techniques aimed at controlling the size and shape of NPs. However, most of these methods utilise toxic and expensive chemicals, and problems are often experienced with NPs stability, agglomeration of particles and the inability to control crystal growth [5]. *Metal nanoparticles* (MNPs) are attracting attention for many technological applications as catalysts, in optical materials, medical treatments, sensors, and in energy storage and transmission. Thus, this type of nanoparticles is topic of our contribution.

Characterization of metal nanoparticles

In general, nanoparticles (10^{-9} m to be precise) are atomic or molecular aggregates with specific physico-chemical properties compared with the bulk material. Currently, nanoparticles have drawn tremendous attention because of their valuable properties on optical, electronic, medical, sensor, and catalytic applications. The synthesis and characterization of metal nanoparticles have emerged as an important branch of nanotechnology in the last decade, particularly for nobel metals such are Au, Pd, Pt and Ag (in detail see [6]). The function and use of these materials depend on their composition and structure [7]. Interest in MNPs currently focuses on control of their size and shape to manipulate their unique optoelectronic, magnetic, catalytic and mechanical properties [8]. A practical route for synthesis of MNPs is by chemical, physical and biological procedures including bacteria, algae and vascular plants. In recent years, the utilisation of biological systems has emerged as a novel technology for synthesis of various nanoparticles in as attempt to control NPs shape, composition, size and monodispersity [9]. While many studies have looked at metal uptake by plants, particularly with regard to phytoremediation and hyperaccumulation, and a few have distinguished between elemental metal deposition (M^0) and metal salt accumulation (M^+), quantification of the proportion of the salts converted to metal nanoparticles has only rarely been addressed [10].

Metal nanoparticle formation and determination

Nanoparticles can be made from variety of bulk materials and they can act depending on chemical composition, size or shape of the particles. Metal nanoparticles are specific type of NPs with unique physical and chemical properties and with different biological effects. One of the most important route for MNPs formation is "green biosynthesis" using not only vascular plants (mainly leaf broth) but also algae, bacteria, yeasts, fungi and actinomycetes. In the field of nanotechnology (including metal/nanoparticles), the controlled synthesis of nanoparticle size, shape and monodispersity is essential in order to explore their unique chemical and physical properties. As it has already been mentioned, there are various chemical and physical methods aimed at controlling the size and distribution of nanoparticles. Most of these methods, however, utilize toxic and expensive chemicals, and problems are often experiences with nanoparticle stability, agglomeration of particles and the inability to control crystal growth [5]. For example, physical synthetic methods such as inert gas condensation, severe plastic deformation, high-energy ball milling and ultrasonic shot peening can be used to synthesize Fe(0) nanoparticles with diameters of 10-30 nm [11]. The chemical methods include microemulsion, chemical coprecipitation, chemical vapour condensation, pulse electrodeposition and chemical wet reduction [11]. On the other hand, in biological methods for preparation of metal nanoparticles mainly leaf reductants occurring in leaf extracts are used (*eg* [12-14]). However, MNPs can be formed also directly in living plants by reduction of the metal ions absorbed as a soluble salt (*eg* [15-18]), indicating that plants are a suitable vehicle for production of MNPs ([19]).

For monitoring of formation and characterization of metal nanoparticles several experimental techniques are applied, such as *UV-Visible spectroscopy* (UV-Vis), *Fourier transform infrared spectroscopy* (FTIR), *transmission electron microscopy* (TEM), *high-resolution transmission electron microscopy* (HRTEM) and *scanning transmission electron microscopy* (STEM), *atomic force microscopy* (AFM), *X-ray diffraction* (XRD), *X-ray absorption near edge structure* (XANES) and *extended X-ray absorption fine structure* (EXAFS) and as well as *X-ray photoelectron spectroscopy* (XPS) (*cf* [20-22]).

Action of metal nanoparticles to living organisms

The toxicity of nanoparticles observed in living organisms can be intrinsic (direct - due to the nanoparticle alone) or indirect (nanoparticle as potential carrier) owing to their proven adsorption potential, which means that there may be pollutants at their surface or within their structure whose toxic potential may be induced, repressed, or limited. Indeed, when they come into contact with the environment, the nanoparticles will be in permanent interaction with the other components of the medium, and in particular, the contaminants.

In some cases, the nanoparticles may play role of collector, *eg* adsorption, for certain molecules, or a masking role wherein they immobilise a non-negligable fraction of the compounds that are potentially reactive for living matter (in detail see [23]).

Papers concerning plant-nanoparticle interactions showed that plants (both vascular and non-vascular) strongly interact with their atmospheric and terrestrial environments and are expected to be affected as a results of their exposure to nanoparticles, including the MNPs. Studies on the toxicity of nanomaterials are still emerging and basically evidence several negative effects on growth and development of plantlets [2]. Toxic effects of MNPs on plants could be connected with chemical toxicity based on the chemical composition (*eg* release of toxic metal ions) and with stress or stimuli caused by the surface, size and shape of the particle. The physico-chemical properties of nanoparticles determine their interaction with living organisms. In general, plant cells possess cell walls that constitute a primary site for interaction and a barrier for the entrance of nanoparticles. Inside cells, nanoparticles might directly provoke either alterations of membranes and other cell structures or activity of protective mechanisms. Indirect effects of MNPs depend on their chemical and physical properties and may include physical restraints, solubilization of toxic nanoparticle compounds, or production of reactive oxygen species. However, it should be stressed that potential risks for health and environment have raised questions on national, European and international levels. Past experience of sanitary, technological, and environmental risks has shown that it is not a good policy to attempt to deal with them after the fact. It is thus crucial to assess the risks as early as possible [24] and thus to avoid serious negative impact of MNPs to environment.

Acknowledgements

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WYSTĘPOWANIE, CHARAKTERYSTYKA I DZIAŁANIE NANOCZĄSTEK METALI

Abstrakt: Nanocząstki metali (MNPS) przyciągają uwagę ze względu na ich wykorzystanie w wielu zastosowaniach jako katalizatory, materiały optyczne, czujniki, w zabiegach medycznych, w przechowywaniu i transmisji energii. Funkcja i zastosowanie tych materiałów zależą od ich składu i struktury. Praktycznymi drogami syntezy MNPS są metody chemiczne i wykorzystanie materiałów biologicznych („zielona synteza” niezawodna, przyjazna środowisku), w tym bakterii, glonów i roślin naczyniowych (głównie metalofitów). Obecnie stosowane są różne fizyczne i chemiczne metody wytwarzania nanocząstek metali i kilka technik eksperymentalnych, mających na celu kontrolę wielkości i kształtu MNPS. Toksyczny wpływ MNPS na rośliny może być związany z toksycznością chemiczną ze względu na ich skład chemiczny (np. uwalnianie jonów metali) oraz stresem lub stymulacją spowodowanymi przez powierzchnię, wielkość i kształt cząstek. Interakcje z organizmami żywymi są określane przez fizykochemiczne właściwości nanocząstek. Ogólnie rzecz biorąc, ściany komórkowe roślin stanowią podstawowy element interakcji i barierę wejścia nanocząstek. Wewnątrz komórek nanocząstki mogą bezpośrednio wywoływać zarówno zmiany błon komórkowych, jak i innych struktur lub spowodować aktywizację mechanizmów ochronnych. Pośrednie skutki MNP zależą od ich właściwości chemicznych i fizycznych, mogących prowadzić do tworzenia pewnych ograniczeń fizycznych, rozpuszczania związków toksycznych czy wytwarzania reaktywnych form tlenu. Jednak należy podkreślić, że wpływ MNPS na zdrowie ludzi i stan środowiska jest nadal niejasny. Z tego względu konieczne jest stworzenie schematu systemu oceny polityki w dziedzinie nanotechnologii (które zostaną wykorzystane do przeglądu całości krajowego planu nanotechnologicznego). Zaproponowano trzy następujące kryteria oceny polityki: adekwatność, efektywność i skuteczność.

Słowa kluczowe: zachowania, skutki bezpośrednie i pośrednie, zielona synteza, organizmy żywe, nanocząstki metali, rośliny

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USE OF A $TiO_2/FeCl_3$ MIXTURE IN ENVIRONMENTAL CLEANING TECHNOLOGY

ZASTOSOWANIE MIESZANINY $TiO_2/FeCl_3$ W TECHNOLOGII OCZYSZCZANIA ŚRODOWISKA

Abstract: One of the methods allowing the use of solar energy being a renewable, alternative form of energy is the environmental cleaning technology. It was stated that many types of pollutants, regardless of their toxicity and resistance to biodegradation, can be effectively degraded in photocatalytic processes initiated by sunlight. Among many different heterogeneous photocatalysts examined, titania (TiO_2) is one of the commonly used in these processes. Unfortunately, in practice the main problem connected with the use of photocatalytic processes is their low quantum yield. In our opinion, the addition of Fe(III) salts to the reaction mixture will be a simple and inexpensive method that increases this yield. It was confirmed in studies on the photocatalytic degradation of many organic compounds, differing in chemical structure and properties. The goal of our study was to compare the results of photocatalytic degradation carried out in the presence of TiO_2 or Fe(III) salts as well in the presence of a mixture TiO_2 with Fe(III) salts. It was found that the ability of organic substrates to form the coordination complexes with Fe(III) ions and their adsorption onto TiO_2 surface has the greatest effect on the course of photocatalytic reaction and its efficiency. Based on the literature data and own studies we propose a probable mechanism of process carried out in the presence of TiO_2/Fe(III) mixture.

Keywords: photocatalysis, TiO_2, environmental cleaning technology

Introduction

One of the methods allowing the use of solar energy is the environmental cleaning technology. It was stated that many types of pollutants, regardless of their toxicity and resistance to biodegradation, can be effectively degraded in photocatalytic processes initiated by sunlight [1-5]. Among many different heterogeneous photocatalysts examined, titania (TiO_2) is one of the commonly used in these processes. Unfortunately, in practice the main problem connected with the use of photocatalytic processes is their low quantum yield and the lack of photocatalytic activity at a wavelength (λ) < 400 nm [1-5].

The subject of TiO_2 activity is widely discussed in scientific journals [1-9]. One of the investigated methods involves extending useful radiation range to visible light. It can be achieved by TiO_2 structure modification by doping with non-metals (like nitrogen, sulfur, fluorine, boron, carbon), platinoids and lanthanides. However, such methods not always are effective and it might increase the cost of catalyst production [1, 8].

In order to sensitize of TiO_2 doping to visible light, Fe^{3+} ions can be used [5, 10-14]. These ions and their partly hydrolysis products may be adsorbed on TiO_2 surface [15, 16]. In our opinion, the addition of Fe^{3+} salts to the reaction mixture containing commercial photocatalyst TiO_2-P25 will be a simple and inexpensive method that increases

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yield of reaction. The addition of Fe^{3+} salts to TiO_2 increases the efficiency of anionic compounds degradation during UVA illumination [10-12, 15-18]. Such effect may be explained by various reasons. There is possible the intensification of sorption process of substrate [16, 17] or the photochemical synergy of TiO_2 and $Fe(OH)^{2+}$ [11]. Additionally, Fe^{3+} ions can take part in light initiated red-ox processes or extending useful radiation range [13-15].

The goal of our study was to compare the results of photocatalytic degradation carried out in the presence of TiO_2 or Fe(III) salts as well in the presence of a mixture TiO_2 with Fe(III) salts.

Materials and methods

Reagents

As model reagents sulfanilamide and its derivates were used. The characteristics of the investigated sulfonamides are presented in Table 1.

Table 1

Characteristics of the investigated sulfonamides

Sulfonamides	**CAS number**	**Abbr. in text**	**pKa_1[a]**	**pKa_2[a]**	**Mobile phase**
Sulfanilamide	63-74-1	SAD	2.4	10.1	AcCN (5%), buffer (K_2HPO_4) pH=8.2
Sulfacetamide	144-80-9	SCT	1.8	5.4	as above
Sulfathiazole	72-14-0	STZ	2.36	7.23	as above
Sulfisoxazole	127-69-5	SSZ	1.5	5.0	as above
Sulfamethoxazole	723-46-6	SMX	1.60	5.81	as above
Sulfadiazine	68-35-9	SDZ	2.00	6.48	as above
Sulfamerazine	127-79-7	SMR	2.1	6.9	as above
Sulfamethazine	57-68-1	SDM	2.3	7.4	AcCN (10%), buffer (K_2HPO_4) pH=8.2
Sulfapyridine	144-83-2	SPY	2.7	8.4	as above
Sulfadimethoxine	122-11-2	SDT	2.9	6.1	as above

[a] $SH_2^+ \xleftrightarrow{Ka_1} SH \xleftrightarrow{Ka_2} S^-$ [20]

All sulfonamides used throughout this study were of analytical grade and were manufactured by Sigma. Just before experiments, 0.1 mmol of each sulfonamide were added to 1 dm^3 of distilled water and samples were intensively mixed. Titanium(IV) dioxide (TiO_2-P25) obtained from Evonic Degussa GmbH and iron(III) chloride ($FeCl_3$) purchased from POCH were used as photocatalysts.

Irradiation

Before irradiation, a solid TiO_2 (500 mg dm^{-3}) and/or 1 cm^3 of $FeCl_3$ stock solution (0.1 mol dm^{-3}) was added to 100 cm^3 samples containing sulfonamides (Table 1). The pH of the irradiated samples was adjusted with concentrated HCl or NaOH solutions (< 1 cm^3). Next, mixtures were homogenized in dark for 30 min by means of magnetic stirrers. In all experiments, open glass crystallizers (volume: 500 cm^3, exposed surface: 102 cm^2) containing the samples were irradiated by UVA lamps (Table 2). The intensity of radiation

(*I*) was measured by Quantum-photo radiometer Delta OHM DO9721. During the irradiation, mixtures were magnetically stirred and were in free contact with the air. The temperature of samples was 21±1°C.

Table 2

The characteristics of radiation sources

Radiation sources	**Abbr., in text**	**Manufacturer**	**The *I* value at the selected λ [W m^{-2})]**		
			< 315 nm^a	**315÷400 nm**	**400÷1050 nm**
4 fluorescent lamps (Actinic BL L40W/10)	UVA lamps	Philips	< 0,02^a	13.6	6.0

[a)] based on manufacturer's data

Analytical methodology

After the appropriate irradiation time the samples were centrifuged (30 min, 4000 RPM). Before and after irradiation, the concentration of sulfonamides in mixtures was determined using HPLC method (column Supelcosil Suplex pKB-100 LC-18, 5 mm, 250 mm x 4.6 mm, detector Waters TAD 486, λ = 254 nm, the characteristics of mobile phases are in Table 1).

Results and discussion

The assessment of photocatalytic degradation dynamics during UVA irradiation

Before the beginning of photocatalytic experiments it was found that in the observed time interval the sulfonamides concentration in samples practically did not decrease as a result of different physicochemical and biochemical processes *eg* hydrolysis, photolysis or biodegradation.

The dynamics of photocatalytic degradation of all investigated sulfonamides (0.1 mmol dm^{-3}) during UVA irradiation of samples in the presence of TiO_2 (0.5 g dm^{-3}) or/and $FeCl_3$ (1.0 mmol dm^{-3}) were also studied. The photocatalytic reactions carried out in the presence of $FeCl_3$ run only in narrow range of pH ~ 3 [11, 17, 18]. Therefore, if necessary, pH of samples was corrected to 3.00±0.05, the samples containing as catalyst TiO_2 only, were irradiated at natural pH and also at pH = 3.

Figure 1 shows the dynamics of this process during UVa irradiation of samples containing the investigated catalysts, using SAD as an example. The plot of function $\ln C_0/C_i = f(t)$ is shown in the upper right corner of Figure 1.

It was stated that during irradiation of samples with $TiO_2/FeCl_3$ the photocatalytic reaction had been inhibited at $C_i/C_0 < 0.15$. The similar effect was observed for all investigated sulfonamides. It was probably caused by the reduction of Fe^{3+} to Fe^{2+} [12, 13, 18, 19]. All experimental results and pH of irradiated samples are presented in Table 3. The photodegradation rate constant (*k*) was calculated based on the linear function $\ln(C/C_0) = f(t)$.

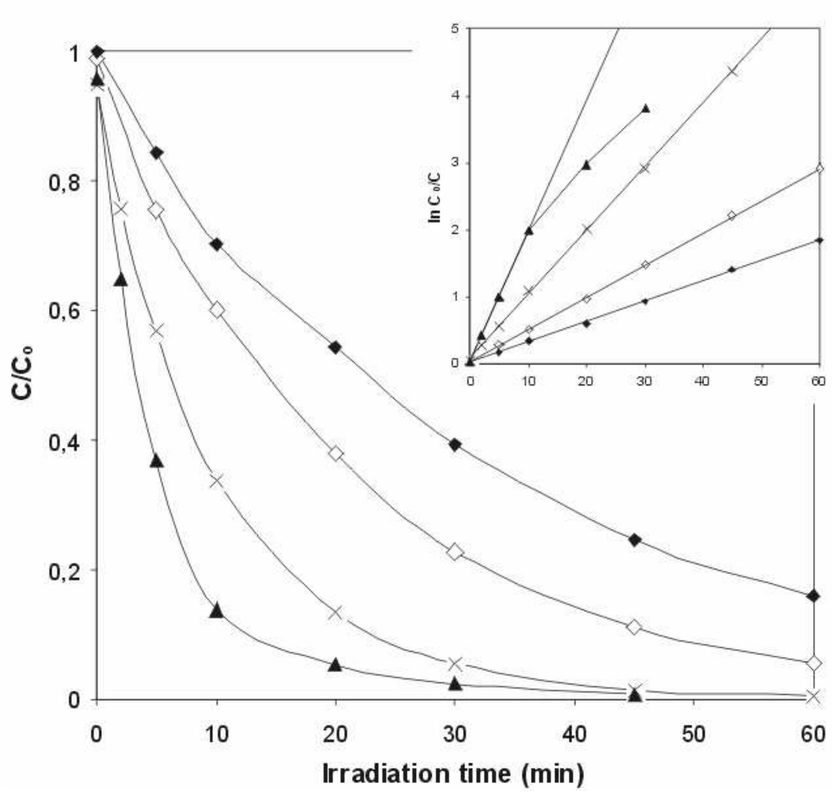

Fig. 1. Degradation of SAD (C_o = 0.1 mmol dm^{-3}) during UVa irradiation in the presence of: ◇ - TiO_2 (pH 6), ◆ - TiO_2 (pH 3), × - $FeCl_3$ (pH 3) and ▲ - $TiO_2/FeCl_3$ (pH 3)

Table 3

The results of experiments

Sulfonamide	**Removal [a] [%]**	***k* [min^{-1}]**			
	Without catalyst	**TiO_2 (pH 4÷8)**	**TiO_2 (pH~3)**	**$FeCl_3$ (pH~3)**	**$TiO_2/FeCl_3$ (pH~3)**
SAD	3.0±1.2	0.048±0.000	0.031±0.000	0.095±0.002	0.197±0.004
SCT	0.0±3.2	0.044±0.001	0.028±0.001	0.074±0.004	0.159±0.008
STZ	0.1±4.5	0.048±0.002	0.051±0.001	0.095±0.002	0.228±0.018
SSZ	5.6±3.3	0.034±0.001	0.035±0.001	0.073±0.003	1.27±0.13
SMX	5.1±3.0	0.033±0.001	0.034±0.001	0.090±0.003	0.121±0.010
SDZ	0.0±1.8	0.032±0.001	0.019±0.001	0.038±0.001	0.146±0.011
SMR	9.5±3.8	0.039±0.001	0.036±0.001	0.068±0.000	0.188±0.009
SDM	3.6±1.5	0.055±0.003	0.052±0.002	0.086±0.002	0.217±0.010
SPY	4.8±1.5	0.050±0.003	0.036±0.002	0.069±0.002	0.141±0.020
SDT	2.4±1.0	0.036±0.001	0.030±0.001	0.062±0.003	0.150±0.013

[a] after 120 min of stirring

It was found that all investigated sulfonamides underwent photocatalytic degradation. The highest activity among the investigated catalysts had $TiO_2/FeCl_3$. Particularly high rate of degradation was observed for SSZ. Under the experimental conditions, just after 150 s of irradiation, about 98% of SSZ was decomposed (data not shown in the text). For comparison, in the same conditions (after 150 s of irradiation and the presence of $TiO_2/FeCl_3$) remaining sulfonamides were decomposed in the range from 26 (SMX) to 51% (STZ). It was stated that the above described degradation of SSZ in the presence of $TiO_2/FeCl_3$ was not caused by photolysis, biodegradation, hydrolysis and stable binding to the components of the catalytic system. A photoactive complex compound of SSZ with Fe also did not form. Unfortunately, we can not explain this anomaly.

The mechanism of photocatalytic process carried out in the presence of $TiO_2/FeCl_3$

Under the investigated conditions, there was no relationship between the rate of photocatalytic degradation of sulfonamides and their rate of acid hydrolysis, photolysis and the presence of chloride ions. Except SMX and SSZ, the *k* value for the reactions carried out in the presence of $TiO_2/FeCl_3$ was from 1.3 to 2.5 times higher than would result from the algebraic sum of k values for reactions carried out separately in the presence of TiO_2 (at pH 3) and $FeCl_3$ (Table 3). The similar effect was described by Mestankova et al [13, 20].

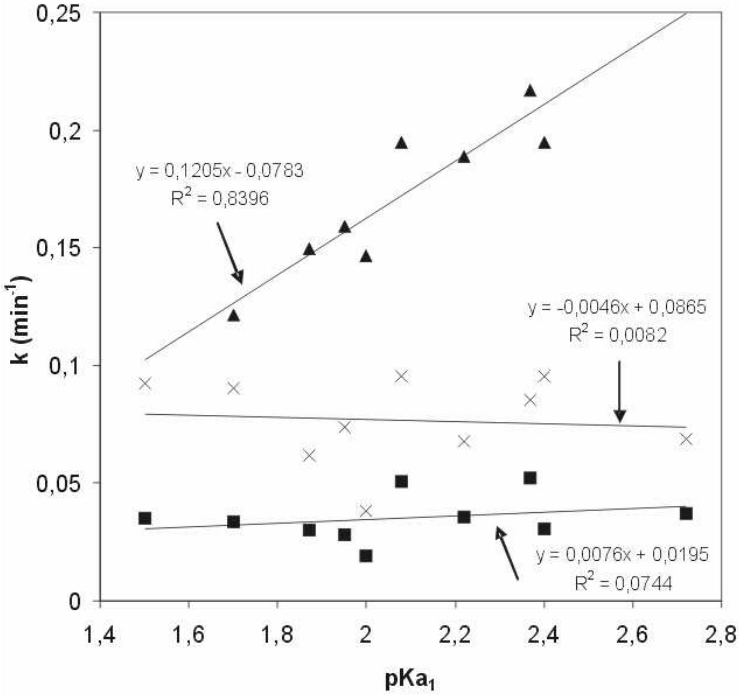

Fig. 2. Effect of the pKa of sulfonamides on the rate of photocatalytic degradation during UVA irradiation in the presence of ■ - TiO_2, × - $FeCl_3$ and ▲ - $TiO_2/FeCl_3$ (this figure does not show the results for the degradation of SSZ and SPY in the presence of $TiO_2/FeCl_3$)

In our opinion, it might be caused by the intensification of sulfonamide sorption on the TiO_2 surface after addition of Fe^{3+} salts to the sample. In darkness, the decrease of sulfonamides concentration was slightly higher in samples with $FeCl_3$ and $TiO_2/FeCl_3$ than in the presence of TiO_2. According to Nahar et al [15], the hydrolysis products of Fe^{3+} ions are adsorbed onto TiO_2 surface. Thus, the compound can be formed as follows:

$$\text{Ti-O-Fe}\leftarrow\text{SH}$$

Both in the anatase as well as in rutile structure each titanium atom is surrounded by six oxygen atoms (negative charges). Therefore, it is possible to form a chemical bond between oxygen atom and the positively charged substrate. In solution at pH 3, sulfonamides occur mainly as neutral molecules (SH) and cations (SH_2^+). Figure 2 shows the relationships between the concentration of the cationic form of sulfonamide and the *k* value for reactions carried out in the presence of TiO_2, $FeCl_3$ and $TiO_2/FeCl_3$, at pH 3.

It was found that in the case of processes carried out with $TiO_2/FeCl_3$ the concentration of SH_2^+ ions was directly proportional to the *k* value (with the exception of SSZ and SPY). There was no correlation in samples containing TiO_2 and $FeCl_3$. Additionally, in most cases a decrease in the pH of samples containing only TiO_2 as catalyst caused a decrease in the photocatalytic reaction rate. These facts indicate that one of the factors affecting the rate of photocatalytic reaction is the simultaneous presence of Fe^{3+} ions and the cationic form of substrate. Thus, it is possible that the essential for the photocatalytic reaction rate in the presence of $TiO_2/FeCl_3$ can be the process shown in Figure 3.

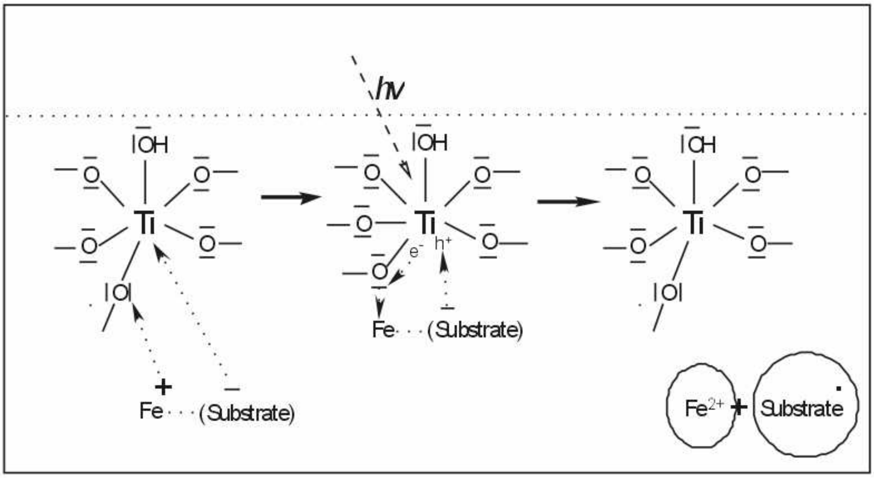

Fig. 3. The mechanism of photocatalytic process carried out in the presence of $TiO_2/FeCl_3$

Conclusions

The addition of $FeCl_3$ to the commercial catalyst TiO_2-P25 significantly increases their photocatalytic activity for UVA irradiation. In the case of sulfonamides, an increase in this activity is directly proportional to the concentration of cationic form the substrate. Assuming the use of sunlight which about 5% of the energy corresponds to a light of wavelength < 400 nm, the application of $TiO_2/FeCl_3$ mixture may be more reasonable than the use of TiO_2 doped with non-metals.

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ZASTOSOWANIE MIESZANINY $TiO_2/FeCl_3$ W TECHNOLOGII OCZYSZCZANIA ŚRODOWISKA

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Abstrakt: Jedną z metod zagospodarowania energii słonecznej jest jej wykorzystanie w technologiach oczyszczania środowiska. W inicjowanych światłem słonecznym procesach fotokatalitycznych mogą być skutecznie degradowane zanieczyszczenia, niezależnie od swojej toksyczności i odporności na biodegradację. Fotokatalizatorem w takich procesach najczęściej jest TiO_2. Niestety problemem tych procesów jest ich niska wydajność kwantowa. Prostą i tanią metodą jej podwyższenia jest dodatek soli Fe(III). Fakt ten potwierdzono w badaniach nad fotokatalityczną degradacją wielu substratów zróżnicowanych pod względem chemicznym. Celem naszej pracy było porównanie rezultatów degradacji fotokatalitycznej prowadzonej w obecności TiO_2, soli Fe(III) i w obecności mieszaniny TiO_2/sól Fe(III) oraz ustalenie mechanizmu procesu fotokatalitycznego prowadzonego w obecności TiO_2/sól Fe(III). Stwierdzono, że na przebieg reakcji i jej efektywność największy wpływ ma zdolność organicznego substratu do tworzenia związku koordynacyjnego z Fe(III) i jego sorpcji na powierzchni TiO_2. Na podstawie danych literaturowych i badań własnych ustalono mechanizm początkowego etapu tej reakcji.

Słowa kluczowe: fotokataliza, TiO_2, technologie oczyszczania środowiska

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PHENOLIC COMPOUNDS IN THE ENVIRONMENT - OCCURRENCE AND EFFECT ON LIVING ORGANISMS

ZWIĄZKI FENOLOWE W ŚRODOWISKU - WYSTĘPOWANIE I WPŁYW NA ORGANIZMY ŻYWE

Abstract: Many of organic compounds used as preservatives in cosmetics, drugs and foods have adverse impact on human and animal health. In recent years, special attention has been paid on substances which interferes with endocrine system of living organisms. The group of this substances is called endocrine disrupting compounds (EDCs) and include wide range of chemicals *eg* phenolic compounds (parabens, phenylphenols, alkylphenols, bisphenol A etc.). EDCs can mimic or block the action of natural hormones causing changes mainly in the reproductive and immune systems, as well tumours formation. Similar to the natural hormones, EDCs are biologically active at very low concentration (pg/g - ng/g), it is the level comparable with their presence in wastewater effluents. Wastewater treatment plants using conventional treatment methods are not effective in removing most of EDCs, therefore, these compounds are present in the environment for example in marine and riverine sediments and surface water, which is often a drinking water reservoir.

Keywords: phenolic compounds, endocrine disrupting compounds, EDCs, parabens, alkylphenols, bisphenol A, phenylphenols

Introduction

In recent years, there has been growing concern about occurrence of commonly used preservatives in aquatic environment and their effect on human and animal health. Special attention has been paid on substances which interfere with endocrine system of living organisms. Group of these compounds is called as *endocrine disrupting compounds* (EDCs). The US Environmental Protection Agency defines EDCs as "an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior" [1]. The list of organic contaminants showing reproductive and endocrine disrupting effects contains: organohalogens, pesticides, phthalates, synthetic steroids, alkylphenols and phytoestrogens [2].

The first cases of the adverse impact of EDCs on living organisms have been observed in the second half of the 20th century, when the declines in seal population occurred in the Baltic Sea and western part of the Wadden Sea were take place. Both of these areas were strongly contaminated with organochlorines. In the next decades the declines in population of many birds species, feminization and intersexuality in fish as well changes in the immune system at marine mammals were reported. EDCs have got ability to bioacumulation and bioconcentration in the food chain, therefore, also people are exposed to their adverse effects. These compounds may cause disturbance in male and female reproduction system *eg* formation of breast and prostate tumours and the endometriosis [3, 4].

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The first action on the issue of EDCs taken by European Union was the workshop "The impact of endocrine disrupters on human health and wildlife", that was held on 2-4 December 1996 in Weybridge. During this workshop a definition of endocrine disrupting compounds was endorsed and the several groups of chemicals which show endocrine properties were identified. Two major group of substances: natural hormones (progesterone, testosterone, phytoestrogens) and synthetically produced hormones (oral contraceptives and synthetic chemicals designed for industrial use) were identified as the most important chemicals causing endocrine disruption [2].

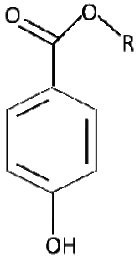
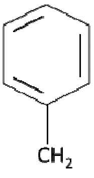
This work is focused on the occurrence of selected phenolic endocrine disrupting compounds in the environment and their effect on living organisms.

Parabens

Parabens (methyl-, propyl-, ethyl-, butylparaben etc.), alkyl esters of *p*-hydroxybenzoic acid (Tab. 1), are commonly used as preservatives in cosmetics, food, pharmaceutical products and personal care products. With the increase of the chain length of the ester groups, antioxidant and antimicrobial activity of parabens increases, while their solubility in water decreases, therefore esters with shorter chain are usually employed [5, 6]. Analysis of cosmetics on the Danish market showed the presence of parabens in 77% of the products at concentration from 0.01 to 0.87%. The maximum concentrations of metyl-, propyl-, etyl-, butyl- and benzylparaben were equal to 0.32, 0.32, 0.19, 0.07 and 0.32%, respectively [7]. Reports of adverse effects of parabens on living organisms caused that use of this preservatives has declined significantly over time. The European Economic Community (EEC) Directive permits the use of parabens in cosmetics with a maximum concentration for each one of 0.4% w/w and a total maximum concentration of 0.8% w/w [8].

Table 1

Chemical structures of selected parabens

Core structure	R	Name
	CH_3	Methylparaben
	CH_2CH_3	Ethylparaben
	$CH_2CH_2CH_2CH_3$	Butylparaben
		Benzylparaben

Widespread use of products containing parabens results in their occurrence in the environment. Many studies have reported the presence of parabens in aquatic environment. These compounds were found in the influent and effluent wastewaters of *Waste Water Treatment Plants* (WWTP) and river waters [9]. The effluents and wastewaters from hospitals and industries (textile manufactures, tanneries, etc.) are considered as the main sources of parabens in the aquatic environment. Parabens concentration in Swedish wastewater is approximately equal to 1 μg/dm^3 [10]. According to the literature, total concentrations of parabens in river waters are diversified from 6 ng/dm^3 [11] to 3204 ng/dm^3 [12], for Glatt River (Switzerland) and Pearl River (China), respectively.

Several *in vivo* and *in vitro* studies have shown that these compounds can mimic the action of natural estrogens such as 17β-estradiol, by binding to the estrogen receptors and influencing the expression of estrogen-dependent genes. The estrogenic activity of parabens increases with the length of alkyl chain [13, 14]. Exposure to *n*-butyl-, *iso*-butyl- and benzylparaben causes increases uterine weights in immature mice [15, 16]. Rodent exposure to butylparaben and propylparaben adversely affected synthesis of the testosterone and male reproductive function [17, 18]. Data on the effects of parabens on human health are limited, and their toxic effects are mostly unknown. Based on the available literature it can be affirm that parabens have got ability to bioaccumulation in the human body. The presence of parabens was confirmed in milk [19], serum [20] and in placental tissue [21]. Moreover, these compounds have been detected in human breast tumor tissue at the ng/g level [22], which may suggest that the use of parabens in deodorants and antiperspirants can increase the incidence of breast cancer.

Alkylphenols

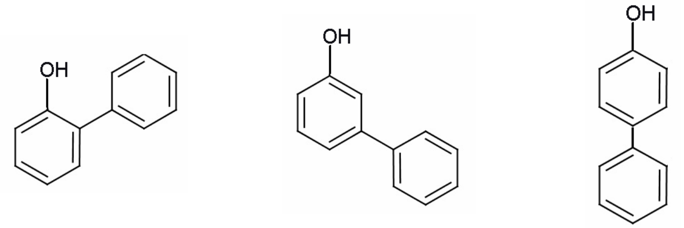
Alkylphenols (octylphenols, nonylphenols etc.) are the main components of *alkylphenol ethoxylates* (APEs), which are nonionic surfactants commonly used as detergents, emulsifiers, wetting agents, plasticizers, UV stabilizers in the herbicides, paints, industrial cleaning and degreasing agents. *Alkylphenols* (APs) are also used as antioxidant and stabilizer of plastics by some industries. The most commercially important alkylphenols are *nonylphenol* (NP) and *octylphenol* (OP) which occur in different forms or isomers [23].

APEs are degraded into APs in wastewater treatment plants, therefore municipal and industrial wastewater treatment plants are main sources of alkylphenols in surface water. The surface water samples contained nonylphenol and octylphenol at concentration equal to 26.4 and 0.68 μg/dm^3 [23], respectively. These compounds were widely detected in sediments [23], as well as in drinking water and food [24]. Amiridou and Voutsa confirmed [25] presence of APs in bottled water. Studies performed on a group of Italians confirmed the presence of seven alkylphenol compounds in the subcutaneous adipose tissue. Nonylphenol was the compound found at the highest level [26]. These compounds were also detected in human milk [27].

APs are persistent environmental pollutants which have been described by European Commission as endocrine disruptors and several of them have been included in the priority list of 33 substances of the *Water Framework European Directive* (WFD) 2000/60/EC [28]. They mimic the action of natural hormones and may interfere with estrogen functions at various reproductive and developmental stages. The highest affinity to the estrogen receptors have been exhibited by mono-substituted alkylphenols with moderate (C4-C6) and long (C8 and C12) alkyl chain length. However, substitution with multiple alkyl groups or presence of substituents in *ortho*- and *meta*- position or lack of hydroxyl group on the benzene ring reduce the binding affinity. APs are known to bioaccumulate and cause cytotoxicity and acute toxicity to aquatic organisms. The cytotoxicity of these compounds increased with their hydrophobicity [29].

Phenylphenols

Phenylphenols (*ortho*-, *meta*- and *para*-phenylphenol), hydroxylated derivates of biphenyl (Fig. 1), have got antimicrobial activity in broad spectrum (efficiency as biocide against bacteria, mold and yeast). *ortho*-phenylphenol has been widely used as a preservative agent for citrus fruits and vegetables, as well in the cosmetics, leather, textile and paper industry. It is also used as a disinfectant in households and hospitals. Multitude of products contain this compound, but the producers uses the trade names of *o*-PP, for example Chemcide, Cotane, Dowicide, Nipacide, among others [30]. *o*-PP is a by-product of the synthesis of phenols and in the microbial desulfurization of dibenzothiophene in fossil fuels [31]. *Meta*- and *para*-phenylphenol are components of the most popular disinfectants used in households [32].



orto-fenylofenol *meta*-fenylofenol *para*-fenylofenol

Fig. 1. The molecular structures of phenylphenols

Wide range of application phenylphenols caused their presence in many parts of the environment. These chemicals were detected in surface water, riverine sediments, sewage sludge [12, 33] and in marine sediments [34]. Studies have shown that phenylphenols are also present in indoor air and dust [35]. Besides, *o*-PP was detected in canned beer and canned soft drinks in United States and Germany. The performed studies indicated on the *o*-PP presence in 49 samples of soft drinks among 55 analyzed samples, at the concentration level of μg/dm^3. The highest concentration *o*-PP was found in a lemon flavored cola, equaled 16.9 μg/dm^3 [30]. Phenylphenols can bioaccumulate in aquatic organisms, *eg* *o*-PP was detected in bile of deep-sea fish at the concentration ranged from 8.4 to 192.7 ng/cm^3 [36].

It was reported that phenylphenols affects the endocrine system, showing estrogenic and antiandrogenic activity. Estrogenicity of phenylphenols strongly depends on the position of the hydroxyl function and increased in the following order: *ortho*- < *meta*- < *para*-phenylphenol [32]. Paris et al observed also that androgen receptors antagonist activity of *ortho*-phenylphenol is 3-4-fold smaller than *meta*- and *para*-phenylphenol [32]. Phenylphenols have got carcinogenic and genotoxic properties [37, 38].

Bisphenol A

Bisphenol A (BPA), 4,4'-dihydroxy-2,2-diphenylpropane (Fig. 2), is a chemical used as stabilizing material for the production of polycarbonate, epoxy resins, unsaturated polyesters resins and polyacrylate and polysulphone resins. Epoxy resins are used in food contact surface lacquer coatings for cans, and in protective coatings and finishes. BPA is also used in resin-based dental sealants and bonding agents [39]. The *specific migration limit* (SML) for BPA from plastic materials to food of 600 ng/g was established by European Commission [40].

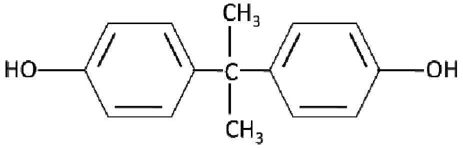


Fig. 2. The molecular structure of BPA

BPA was found in river water at the concentrations ranged from 0.06 to 0.33 μg/dm^3 [39]. Significant levels of this compound was detected in fish and shellfish. Averaging concentrations of BPA in crabs and squid were equalled to 213 and 118 μg/kg, respectively [41]. It was also detected in human blood [20].

BPA is an endocrine disruptor, showing estrogenic and antiandrogenic activity leading to the interference of reproductive system. BPA is able to activate estrogen receptors at concentration lower than 1 μM [32]. This compound has been also classified as carcinogenic and mutagenic, producing adverse effects on animal, aquatic life and human health [40]. Broad applications of BPA caused this compound can enter into human body by ingestion or adsorption. Exposure to BPA during the early stage of pregnancy can seriously affect the embryonic development and maintenance of pregnancy. Exposure fetuses, infants and children to BPA may effect on development of the prostate gland and brain and behavioral effects [42].

Conclusions

Widespread application of phenolic compounds has caused the spread of these chemicals in the environment. They have been detected in wastewater influents and effluents, surface waters, and in riverine and marine sediments. Wastewater treatment plants using conventional treatment methods are not effective in removing most of these compounds, therefore, they are considered as the main sources of phenolic compounds in surface water.

Many of phenolic derivatives (parabens, alkylphenols, bisphenol A, phenylphenols etc.) interferes with endocrine system of living organisms, causing disturbance in male and female reproduction system *eg* formation of breast and prostate tumours and the endometriosis. Due to the ability of EDCs to bioaccumulation and bioconcentration in the food chain also people are exposed to their adverse effects. Therefore, in order to limit human exposure to phenolic compounds, releasing these chemicals into environment should be definitely reduced.

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ZWIĄZKI FENOLOWE W ŚRODOWISKU - WYSTĘPOWANIE I WPŁYW NA ORGANIZMY ŻYWE

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Abstrakt: Wiele związków organicznych stosowanych jako środki konserwujące w kosmetykach, lekach i żywności niekorzystnie wpływa na zdrowie ludzi i zwierząt. W ostatnich latach szczególną uwagę naukowców na całym świecie zwracają związki chemiczne, powodujące różnego rodzaju zakłócenia w układzie hormonalnym organizmów żywych. Do związków tych, określanych mianem syntetycznych związków endokrynnych (*endocrine disrupting compounds* - EDCs), zalicza się m.in. szeroką gamę pochodnych fenolowych (np. parabeny, fenylofenole, alkilofenole, bisfenol A) i wiele innych. Związki endokrynne mogą naśladować lub blokować działanie naturalnych hormonów, powodując zmiany w układzie rozrodczym, immunologicznym oraz powstawanie nowotworów, co w konsekwencji prowadzi do poważnego zachwiania równowagi ekologicznej. EDCs, podobnie jak ich naturalne odpowiedniki, wykazują aktywność hormonalną już przy bardzo niskich stężeniach, rzędu pg g^{-1} i ng g^{-1}. Większość oczyszczalni ścieków nie jest przystosowana do wydajnego usuwania EDCs ze strumienia ścieków, dlatego też związki te są obecne w wielu elementach środowiska, m.in. w osadach rzecznych i morskich, jak również wodzie powierzchniowej, będącej często rezerwuarem wody pitnej.

Słowa kluczowe: związki fenolowe, ksenoestrogeny, EDCs, parabeny, alkilofenole, bisfenol A, fenylofenole

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SEWAGE SLUDGE AS AN ENVIRONMENTAL FRIENDLY ENERGY SOURCE

OSADY ŚCIEKOWE ŹRÓDŁEM ENERGII PRZYJAZNEJ ŚRODOWISKU

Abstract: The predominant method of the sewage sludge management in Poland is land disposal. However, since 01.01.2013, this method will be prohibited. Therefore, there is a strong need for development of thermal methods of sludge disposal. In the Polish legal system sewage sludge may be named as a biomass or waste. For purposes of determining the obligations of environmental regulations definition of the Minister of Environment should be used. When disposing of sewage sludge in an amount up to 1% by weight of fuel, emission standards for fuel do not change. At the disposal of sewage in quantities of more than 1%, should be conducted continuous measurement of emissions, including HCl, HF, and continuous measurements of flue gas parameters (as for the installation of waste disposal). For purposes of settlement of the share of energy from renewable sources we use the definition of Minister of Economy. In this case, in accordance with applicable law sewage sludge shall be considered as pure biomass is CO_2 neutral. The use of sewage sludge as a fuel requires the determination of fundamental combustible properties. These properties should be in accordance with the requirements put fuels as an energy source. The paper presents results of a detailed physico-chemical analysis of dried sewage sludge produced in the two Polish wastewater treatment plants. The results were compared with five representatives of biomass fuels: straw of wheat, straw of rape, willow, pine and oak sawdust. Ultimate and proximate analysis includes a detailed analysis of fuel and ash. The results clearly indicate that the sludge is a very valuable fuel similar to "traditional" biomass.

Keywords: sewage sludge, thermal treatment, combustible properties

Introduction

Sewage sludge, originating from the treatment process of wastewater, is the residue generated during the primary (physical and/or chemical), the secondary (biological) and the tertiary (additional to secondary, often nutrient removal) treatment [1-3]. Removal of sludges from *Wastewater Treatment Plants* (WWTP) represents a serious worldwide environmental problem. Not long ago, it was thought that raw sludge was a valueless material that should be discarded, and then it was disposed of in landfills and/or thrown into the ocean. But the huge amounts of sludge produced make all these options environmentally unacceptable. The high output of sewage sludge, which is increasing during recent years, and the limitations of the existing means of disposing sewage sludge highlight the need to find alternative routes to manage this organic material. The *6th Environment Action Programme 2002-2012* of the European Commission has been described as a major factor in reducing sewage sludge disposal by 50% from 2000 by 2050. Moreover, European legislation prohibits the deposition of sewage sludge into landfill or water. Biomass and residues like sewage sludge are the only renewable energy sources that can provide C and H, thus it is interesting to process them by means of treatments that enable to obtain chemically valuable products like fuels. As a type of biomass fuel, sewage sludge is a renewable source and has advantage of being CO_2-neutral: no additional CO_2 is estimated into the atmosphere in the long term. The latest trends in the field of biomass and

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sludge management, (*ie*, combustion, pyrolysis, gasification and co-combustion) have generated significant scientific interest [4]. Gasification is the process of converting a solid fuel into a gas by treating the solid fuel in a generator with oxygen, air, and steam or by other gasification methods [5]. As shown by Marrero et al, gasification of sewage sludge leads to a high-quality flammable gas that can be used for the generation of electricity or to support such processes as the drying of sewage sludge [6]. Gasification is one way of using sewage sludge and is an attractive alternative to other treatment methods. To determine the usefulness of sewage sludge as a biomass fuel for thermal transformation, it is necessary to know its basic physical and chemical characteristics. The elemental composition of sewage sludge and the contents of inorganic compounds depend on many factors, but it may be largely dependent on the country or region of origin.

The aim of the work is comparison of physico-chemical properties of dried sewage sludge produced in the two Polish wastewater treatment plants with five representatives of "traditional" biomass fuels: straw of wheat, straw of rape, willow, pine and oak sawdust. Ultimate and proximate analysis includes a detailed analysis of fuel and ash.

Results

Within this study straw of wheat and rape, oak, willow and pine sawdust and two sewage sludge samples were examined. The proximate and ultimate analyses are presented in Figure 1.

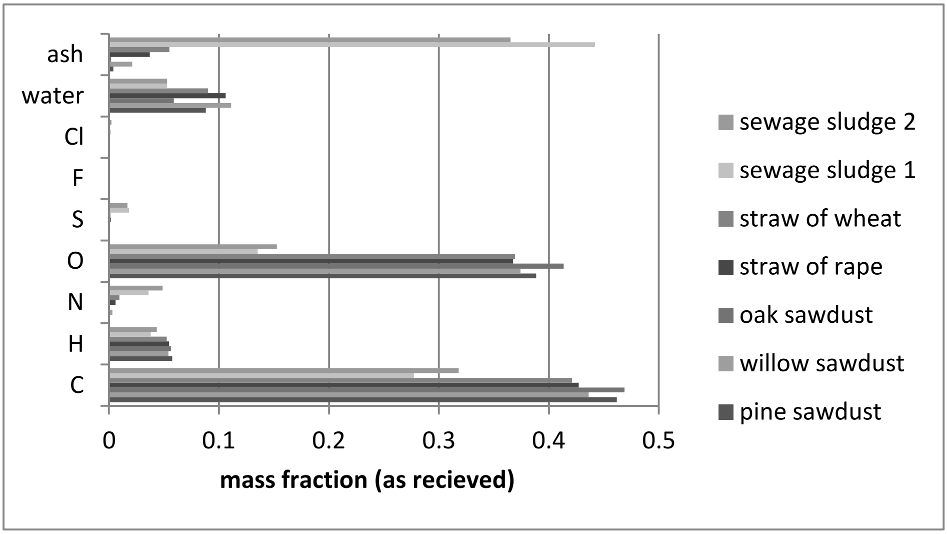

Fig. 1. Ultimate analysis and ash and water content in analysed feedstock

The moisture of the feedstock was obtained following standard PN-EN 14774-3:2010 [7]. The infrared spectroscopy analyzer was used to carry out the ultimate analysis of the sewage sludge.

The volatile matter content was determined according to standard PN-EN 15402:2011 [8]. The ash content was obtained using PN-EN 15403:2011 [9]. The calorific content was determined in accordance with standards CEN/TS15400:2006 [10].

As it can be seen from ultimate analysis, there are no significant differences in the C, H, Cl and F content. Nevertheless, taking into consideration S, N and O contents that difference between “traditional” biomass and sewage sludge is quite strong. Despite the fact that sewage sludge contains phosphorus, nitrogen and sulfur, the gasification of these components offers several advantages over a traditional combustion process. Gasification takes place in an environment with low levels of oxidizers (to prevent the formation of dioxins) and large quantities of sulfur and nitrogen oxides [11]. As mentioned above, sulfur is present in sewage sludge at low amounts; it is mainly converted to hydrogen sulfide (H_2S) during gasification [12], whereas the nitrogen is transformed into ammonia [11].

It is worth noting that the phosphorus in sewage sludge is partitioned into solid (not gaseous) residues [13] and that the volume of syngas produced from sewage sludge is low because gasification requires a fraction of the stoichiometric amount of oxygen necessary for combustion. For all of these reasons, gasification requires smaller and less expensive gas-cleaning facilities [14-16]. Analysing Figure 1 it can be also seen that the sewage sludge were characterized by higher ash content than “traditional” biomass feedstock.

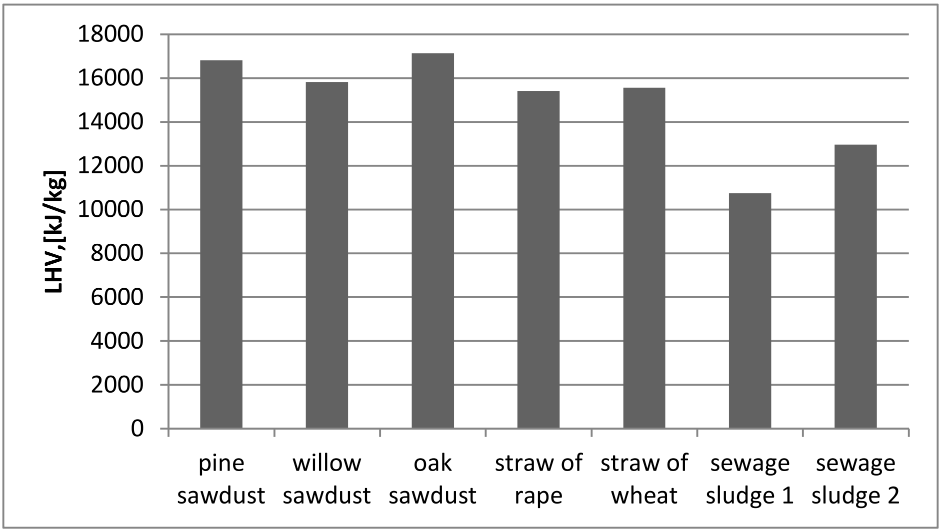

Fig. 2. Lower heating value of analysed feedstock

It can be seen in Figure 2 that lower heating value is comparable to that of traditional biomass. Simultaneously in Figure 3, it can be observed that volatile matter content in the sewage sludge is much lower in comparison with traditional biomass. The combination of low oxygen content and low volatile matter in sewage sludge indicates a low potential for creating large amounts of inorganic vapors during combustion and another thermal processes.

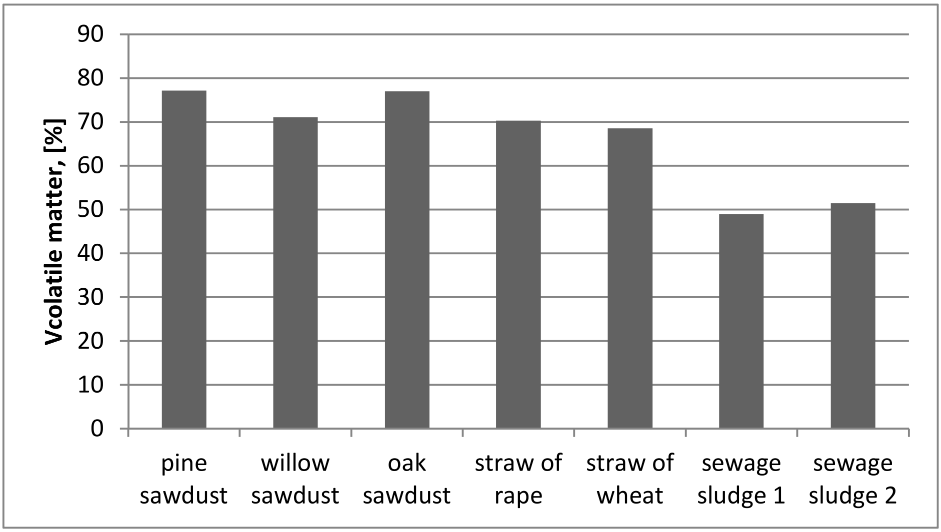

Fig. 3. Volatile matter content of analysed feedstock

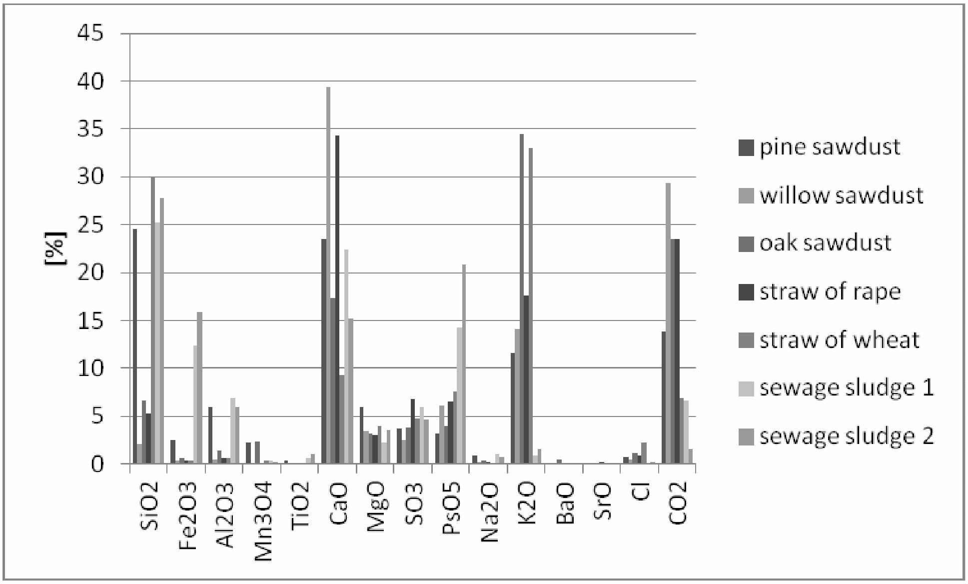

Fig. 4. Ash chemical analysis of analysed feedstock

The results of the chemical analyses of the fly ashes are presented in Figure 4. The plasma spectrometer Thermo iCAP 6500 Duo ICP was used to carry out the ash analysis of the biomass feedstock.

Ash behavior and deposition tendencies were predicted through the use of empirical indices for biomass type ashes [17-19]. These indices, despite their shortcomings due to the complex conditions, which arise in boilers and their associated heat transfer equipment, are widely used and probably remain the most secure basis for decision making, if used in conjunction with pilot plant testing.

One simple index, the alkali index (*AI*) which is a parameter frequently used to describe the overall influence of catalytically active species within the ash and is defined as the ratio of the sum of the fraction of the basic compounds in the ash (CaO, MgO, K_2O, Na_2O and Fe_2O_3) to the fraction of the acidic compounds (SiO_2 and Al_2O_3) in the ash, multiplied by the ash value:

$$AI = ash\% \cdot \frac{\mathrm{CaO} + \mathrm{MgO} + \mathrm{K_2O} + \mathrm{Na_2O} + \mathrm{Fe_2O_3}}{\mathrm{SiO_2} + \mathrm{Al_2O_3}} \tag{1}$$

When the *AI* increases slagging tendency increases.

Another index, the base-to-acid ratio ($R_{b/a}$) - eq. (2). As $R_{b/a}$ increases, the fouling tendency of a fuel ash increases:

$$R_{b/a} = \frac{\%(\mathrm{CaO} + \mathrm{MgO} + \mathrm{K_2O} + \mathrm{Na_2O} + \mathrm{Fe_2O_3})}{\%(\mathrm{SiO_2} + \mathrm{TiO_2} + \mathrm{Al_2O_3})} \tag{2}$$

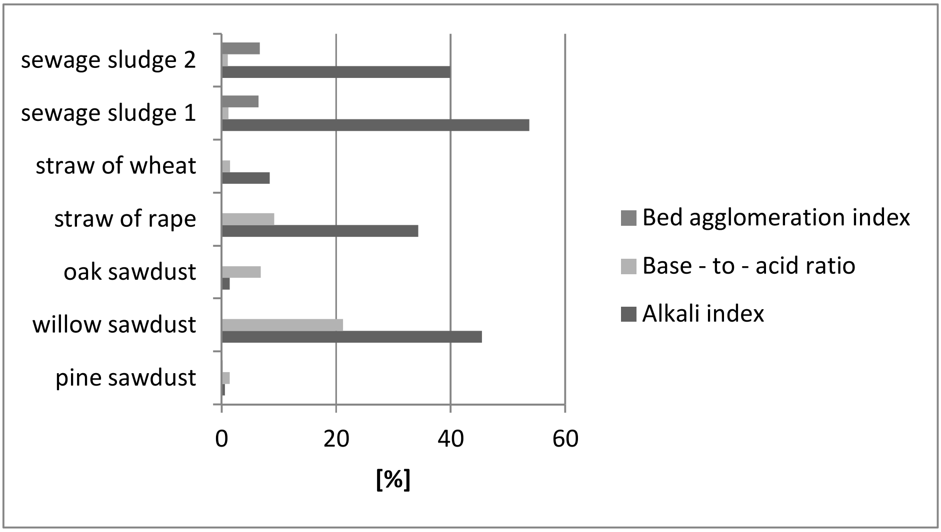

Fig. 5. Slagging/fouling indexes of analysed feedstock

A bed agglomeration index (*BAI*) - eq. (3) has been developed, relating ash composition to agglomerations in fluidized bed reactors:

$$BAI = \frac{\%\mathrm{Fe_2O_3}}{\%(\mathrm{K_2O} + \mathrm{Na_2O})} \tag{3}$$

Bed agglomeration occurs when *BAI* values become lower than 0.15. Analysing data presented in Figure 5 it can be concluded that sewage sludge is characterizing by higher slagging tendency in comparison with traditional biomass (especially oak and pine sawdust). Simultaneously sewage sludge ash is characterised by lower fouling tendency than traditional biomass ash and higher tendency to create agglomerates.

Conclusions

The analysis of various biomass materials indented to be used as supplemental fuel in fossil fuel fired power plants has shown that there is always a range of the results sometimes with a big gap between minimum and maximum. Most noticeable for the sewage sludge was the highest share of ash, nearly 50% of the dry substance, compared with all the other fuels. Additionally it should be emphasis that the combination of low oxygen content and low volatile matter in sewage sludge indicates a low potential for creating large amounts of inorganic vapors during combustion and another thermal processes. Moreover, sewage sludge is characterizing by higher slagging tendency, lower fouling tendency and higher tendency to create agglomerates in comparison with traditional biomass.

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OSADY ŚCIEKOWE ŹRÓDŁEM ENERGII PRZYJAZNEJ ŚRODOWISKU

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Abstrakt: Dominującym kierunkiem zagospodarowania osadów ściekowych w Polsce jest ich składowanie. Jednakże od 1.01.2013 r. sposób ten będzie zabroniony. Istnieje zatem silna potrzeba rozwoju termicznych metod utylizacji osadów. W polskim ustawodawstwie osad może być nazywany biomasą lub odpadem. Dla celów ustalenia, jakie obowiązki wynikają z przepisów ochrony środowiska, korzystać należy z definicji Ministra Środowiska. Przy utylizacji osadów ściekowych w ilości do 1% masy paliwa standardy emisyjne dla paliw nie ulegają zmianie. Przy utylizacji osadów w ilości ponad 1% należy prowadzić ciągły pomiar emisji zanieczyszczeń, w tym HCl i HF, a także ciągły pomiar parametrów spalin (jak dla instalacji utylizacji odpadów). Na potrzeby rozliczenia udziału energii pochodzącej ze źródeł odnawialnych stosuje się definicję Ministra Gospodarki. W takim przypadku, zgodnie z obowiązującym prawem, osady ściekowe uznaje się za czystą biomasę neutralną pod względem CO_2. Wykorzystanie osadów ściekowych jako paliwa wymaga określenia podstawowych właściwości palnych. Parametry te powinny odpowiadać wymaganiom, jakie są stawiane paliwom w celu ich energetycznego wykorzystania. W pracy przedstawiono wyniki szczegółowej analizy fizykochemicznej suszonych osadów ściekowych wytworzonych w dwóch polskich oczyszczalniach ścieków. Wyniki zostały porównane z pięcioma rodzajami paliw biomasowych: słomy pszennej, rzepakowej, wierzby energetycznej, trocin sosnowych i dębowych. Analiza obejmowała skład elementarny paliw oraz szczegółową analizę popiołu. Wyniki jednoznacznie wskazują, iż osady ściekowe są bardzo wartościowym paliwem, nieróżniącym się w zasadniczy sposób od „klasycznej” biomasy.

Słowa kluczowe: osady ściekowe, termiczna utylizacja, własności palne

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ULTRASONIC STABILIZATION OF THE ACTIVATED SLUDGE SAMPLES FOR PARTICLE SIZE DISTRIBUTION PSD MEASUREMENTS USING LASER DIFFRACTION METHOD

ULTRADŹWIĘKOWA STABILIZACJA OSADU CZYNNEGO W POMIARACH ROZKŁADU WIELKOŚCI CZĄSTEK PRZY WYKORZYSTANIU METODY DYFRAKCJI LASEROWEJ

Abstract: Laser diffraction method is one of recently applied method for measurement of active sludge particles size distribution. This method requires mixing of the suspension and then pumping it through the measurement unit. Energy of mixing and process of pumping may destroy flocks of the active sludge and change its properties during the measurement. Thus, stabilization of the active sludge flocks before measurement is required. The purpose of this paper was to determine the possibility of flocks sample stabilization for measurements with application of laser diffraction method. This stabilization should allow comparison of various sludge flocks' diameters, obtained in different conditions. Resuming our results, we may state that according to practical application, usage of stabilization based on ultrasounds was sufficient. However, in order to obtain the replicable results for various types of the active sludge it is necessary to precise describe the ultrasound energy provided to flocks before the measurement.

Keywords: laser diffraction method, activated sludge particles diameter, stabilisation of the activated sludge by sonication

Physical parameters of an active sludge, in particular its flocks diameter have significant effect on the proper operation of bioreactor chambers and secondary sedimentation tanks of wastewater treatment plants. Parameters connected with size of activated sludge flocks are also resulting from the species composition of active sludge organisms and may inform about possible malfunction of biological part [1-3]. Measurement of the dimensions of an active sludge flocks may be conducted in many ways [4-6]. Microscopic methods were used as one of the first [4, 7, 8]. However, time-consuming application of microscopic analyses resulted in search for the other methods, allowing quick and precise measurements. One of the methods recently gaining popularity in flocks dimensions measurements is laser diffraction [6, 9-13].

Description of particle size distribution by the laser diffraction method is based on measurement of light intensity dispersed on particles located in measuring unit - the smaller particle, the larger angle of dispersion is. Though, the particle size distribution obtained in this method is a volumetric distribution (informing about the share of given granulometric faction in the total volume of the sample), various then mass distribution (portion of a given faction mass in the mass of a whole sample) obtained by methods based on sedimentation process [14]. Assuming that the spherical shape of all particles (for both sedimentation and laser diffraction methods) and identical densities the volumetric particle distribution agrees

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with mass distribution. Recently used laser diffractometers have relatively wide measurement range - from fractions of micrometers to several millimeters. According to this wide range, in particular measurements of the larger particles, the dynamic flow of measured suspension through the measuring unit is required.

Lack of mixing and pumping of suspension through measurement installation would result in sedimentation and leaving the measurement range by the following fractions. In order to laser diffractometer construction (various models of different producers) the structure/composition of mixing units may vary. Volume and shape of reservoir, construction of stirrer, integration (or its lack) of stirrer and pump result in delivering various amount of energy to the mixing suspension. On the other hand, high intensity of mixing may result in incidence of bubbles of air in fluid body, which may be treated by measuring unit as measured particles agglomeration [15].

The dynamic mixing and pumping may also effect the properties of measured particles. This situation occurs during studies over particle size distribution of the active sludge. Any type of mixing causes destruction of spatial structure of the sludge. Thus, it becomes that dynamic of mixing will affect on rate and range of structures decomposition.

The aim of this paper was to determine the possibility of samples stabilization applicable to laser diffraction method to avoid changes of samples properties during the measurements. This stabilization could simultaneously allow comparison of diameters of various sediments, obtained in different process conditions or sampled in different points/units of biological part of wastewater treatment plant.

Materials and methods

Method

The measurements were performed using laser diffractometer Mastersizer 2000, Malvern, UK, with Hydro MU dispersion unit. The measuring range for material analysed in liquid dispersion was 0.02÷2000 μm. The Mie theory was applied for recalculations of light intensity measured on detectors into PSD of the activated sludge. According to the Mie theory the identification of optical parameters is necessary. The value of light refraction index for the continuous phase was set as for water (1.33). The values for dispersed phase were assumed as follows: index of refraction for light - 1.53, and absorption coefficient - 0.1. The assumed optical parameters can be must be treated as average when the measured mixture is heterogeneous [15].

Materials

Activated sludge sampled at a municipal *waste water treatment plant* (WWTP) with a capacity of approx. 80 000 m^3/day and employing C, N and P treatments served as the test material in the presented study. The sludge was sampled from the aeration chambers using 1.5 dm^3 containers.

Sample preparation

Samples of the activated sludge were prepared using sonication. Exposure duration of sonication covered the time of 4 minutes and the power of the applied ultrasound probe was 35 W (maximum power of ultrasound probe built in the device).

Measuring procedure

The measurement in Hydro MU unit was carried in 1000 cm^3 beaker which was filled in about ¾ of the maximum volume. The speed of stirrer and pump (the stirrer and pump are integrated in Hydro MU dispersion unit) was 1200 rpm.

Each measurement of particle size distribution was conducted as a series of 20 replications. A single measurement was adopted as 30,000 counts registered on the detectors during 30 seconds for red as well as for blue light. Hence, the duration of a single measurement was equal to one minute. The measurement replications were realized in a sequence, so the measurement time for one full studied series was equal to 20 minutes.

Mean values were not calculated for the results obtained for the 20 replications because it was assumed that intensive stirring and pumping might disintegrate the studied flocks. The change of the median in the subsequent measurements (from the 1st to the 20th) was the measure of the disintegration of the flocs made by the stirrer and pump.

The volume of sludge used for the measurements was determined by *obscurance* - a parameter measured by the device during the dosing process. With respect to measurement reliability, the number of particles for which the *obscurance* parameter value covers the range of 10 to 20% is optimal [16]. Concentration of the studied suspension, obtained directly from the wastewater treatment plant, was too high, so the suspension was added to filtered water to obtain the recommended standard of the *obscurance* parameter. When because of overdosage of suspension to the measuring system obscuration was too high the procedure of dilution was used [17].

Results and discussion

The change of the median in the subsequent measurements (from the 1st to the 20th) is presented in Figure 1.

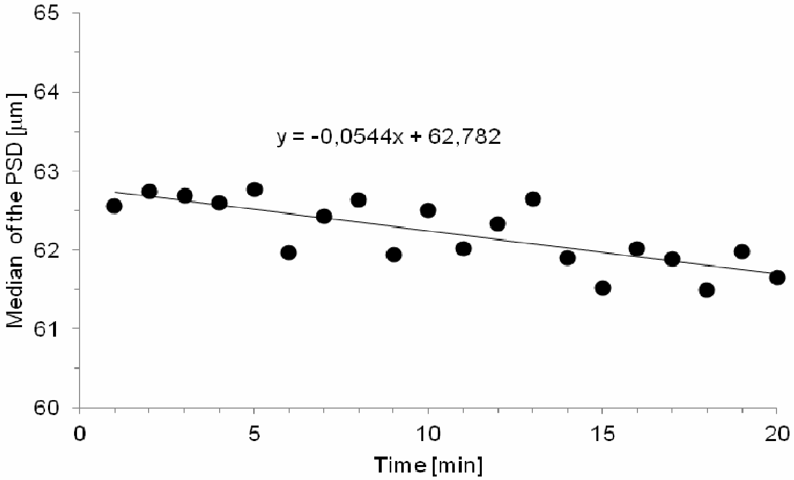

Fig. 1. The change of the median in the subsequent measurements (from the 1st to the 20th). Each single measurement lasted one minute

The distinct decrease of the values of flock diameter medians from 62.55 μm to 61.65 μm can be observed in Figure 1. It means that 4 minutes of ultrasounds before the measurement is not enough to definitively stabilize size of the flocks and the stirring and pumping has are still able to break them. However the changes of the median are small - less than 1.5% during 20 subsequent measurements. Additional argument for the small decrease of the flocks size is the small value of slope (–0.05). It seems that for the practical purposes this change can be neglected the more so the first few median values were nearly the same and there was not the decrease. This is consistent to the other our researches [18].

Summary and conclusions

1. The ultrasound can by the good way for preparation of the activated sludge for PSD measurements.
2. The energy of ultrasounds should be established very precisely if one wants to compare the results oft he PSD for different sludge samples.

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ULTRADŹWIĘKOWA STABILIZACJA OSADU CZYNNEGO W POMIARACH ROZKŁADU WIELKOŚCI CZĄSTEK PRZY WYKORZYSTANIU METODY DYFRAKCJI LASEROWEJ

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Abstrakt: Jedną z metod ostatnio wykorzystywanych do pomiaru rozkładu wielkości cząstek osadu czynnego jest metoda dyfrakcji laserowej. W metodzie tej konieczne jest mieszanie mierzonej zawiesiny w celu homogenizacji próbki, a następnie przepompowywanie jej przez układ pomiarowy. Energia mieszania i pompowanie mogą rozbijać kłaczki osadu czynnego, przez co zmieniać jego właściwości w czasie pomiaru. Dlatego też niezbędna jest stabilizacja cząstek osadu czynnego przed realizacją pomiaru. Celem niniejszej pracy było określenie możliwości stabilizacji próbki kłaczków osadu czynnego w pomiarach z wykorzystaniem dyfrakcji laserowej. Stabilizacja taka miałaby umożliwić porównywanie ze sobą wielkości (średnic) różnych osadów, uzyskiwanych w różnych warunkach. Podsumowując wyniki, należy stwierdzić, że do celów praktycznych wystarczająca jest stabilizacja przy wykorzystaniu ultradźwięków. Jednakże, aby umożliwić porównywalność wyników uzyskiwanych dla różnych osadów, niezbędne jest dokładne określenie energii ultradźwięków, którymi kłaczki są stablizowane przed pomiarem.

Słowa kluczowe: metoda dyfrakcji laserowej, średnica cząstek osadu czynnego, stabilizacja osadu ultradźwiękami

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ACCUMULATION OF SELENIUM BY WINTER WHEAT (*Triticum aestivum* L.) AS THE RESULT OF LONG-TERM FARMYARD MANURE FERTILIZATION

AKUMULACJA SELENU PRZEZ PSZENICĘ OZIMĄ (*Triticum aestivum* L.) POD WPŁYWEM WIELOLETNIEGO NAWOŻENIA NAWOZEM NATURALNYM

Abstract: The objective of this study was to determine the selenium content in soil and its accumulation and distribution in winter wheat plants affected by organic fertilization. There was found a significant effect of FYM application on the total selenium in soil. The total selenium content in soil was significantly correlated with organic carbon content. The highest selenium concentrations were observed in aboveground biomass of winter wheat gathered from plots treated with FYM with the doses of 20 and 40 Mg · ha^{-1}, which was about 70% higher in comparison with the control plants. The selenium content in winter wheat roots from the control plots was on average above 30% higher than from the FYM plots.

Keywords: selenium, soil, winter wheat, organic fertilization

The concentration of selenium in plants depends on the chemical form of Se, its concentration and bioavailability in soils and on the accumulation capacity of the plant [1]. Although all the plants are able to take up and to metabolize selenium, the assumption about its necessity for plants has not been fully confirmed yet. Numerous studies have shown that at low concentrations Se exerts a beneficial effect promoting growth and increasing stress tolerance of plants by enhancing their antioxidative capacity, reducing lipid peroxidation and enhancing the accumulation of starch and sugars [2-4]. Higher plants vary in their capacity to accumulate and tolerate selenium and they are classified into non-accumulators, indicators and accumulators [5]. According to Whanger [6], the currently observed interest in selenium focuses on the health benefits of high-Se plants as a source of cancer-preventative Se compounds, for its unique role in recycling and delivering selenium from the soil to the food chain. The objective of this study was to determine the selenium content in soil and its accumulation and distribution in winter wheat plants affected by organic fertilization.

Materials and methods

Soil and plant samples were taken from a long-term static field experiment carried out since 1980 by the Department of Plant Nutrition of the Institute of Soil Science and Cultivation in Pulawy in the area of the Agricultural Experimental Station at Grabow on the Vistula River. Soil samples were collected in the 22nd year of the experiment, in May 2002, from the 0-20 cm layer in the winter wheat interrows (cv. Korweta). The experiment was designed in a split-plot with four replications. Crop rotation included: potato - winter wheat + intercrop - spring barley + undersown and red clover + grasses. The soil was treated with

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cattle *farmyard manure* (FYM) under potato in the doses of 0, 20, 40, 60 and 80 Mg·ha^{-1}. Plant material was sampled at the beginning of the shooting stage into blade, rinsed in deionised water to remove soil particles, separated into aboveground biomass and roots, and dried. The total selenium content in soils and plants was determined using the method of Watkinson [7] with a Hitachi F-2000 spectrofluorometer. The analytical procedures provided satisfactory values for the standard reference material CRM024-050 (RTC). The soil samples were analysed for granulometric composition according to Bouyoucos-Casagrande method, organic carbon - using wet oxidation with potassium dichromate, and pH in distilled water and 0.1 M KCl - potentiometrically.

Results and discussion

The general properties of the soil under study are given in Table 1. The soil, according to the FAO classification, was classified as Haplic Luvisols and demonstrated the texture of loamy sand and sandy loam. The soil pH values were found in the slightly acidic range 5.7-6.2. The application of manure resulted in the highest amounts of organic carbon in soil, especially in soil from the plots fertilized with FYM with the doses of 60 and 80 Mg · ha^{-1}. The selenium content from the control plots ranged from 0.086 to 0.117 mg · kg^{-1} (average 0.101 mg · kg^{-1}) (Table 1). Statistical analyses confirmed that the FYM application resulted in the highest amounts of total selenium content in soil (Table 1), which increased with increasing doses of manure. The soil fertilized with the highest dose of manure showed a two-fold higher rate of total selenium than the soil from the control plots, which could have been due to the amount of this microelement in farmyard manure since, as reported in literature, in various FYM the selenium content varies from 0.32 to 2.4 mg · kg^{-1} [8, 9].

Table 1

General properties and total selenium content in soil under study

Dose of manure [Mg · ha^{-1}]	**Soil particle size fraction [%]**		**pH**		**Organic carbon [g · kg^{-1}]**	**Total Se [mg · kg^{-1}]**
	< 0.02 mm	**< 0.002 mm**	**H_2O**	**KCl**		
0	18	7	6.2	5.8	8.6	0.099
20	16	7	6.2	5.8	9.9	0.171
40	17	6	6.0	5.7	10.3	0.179
60	18	6	6.2	5.8	10.6	0.184
80	15	5	6.2	5.8	11.1	0.191
						LSD $_{0.05}$ 0.010

According to Kabata-Pendias [3], the mean total selenium content in the soils worldwide is estimated as 0.44 mg · kg^{-1}, while its background contents in various soil groups range from 0.05 to 1.5 mg · kg^{-1}. Hartikainen [2] claim that soils containing less than 0.5 mg Se · kg^{-1} are likely to lead to crops and pastures with inadequate selenium concentrations (< 0.05 mg · kg^{-1} d.m.). The total selenium content in soil under study was significantly correlated with the organic carbon content, which coincides with our earlier findings [10] and those reported by other authors [3, 8, 11]. Navarro-Alarcon and Cabrera-Vique [12] report on selenium levels in soil generally being reflected in food and the Se levels in human populations. In the present study the average selenium content in upper parts of winter wheat from control plots reached 0.133 mg · kg^{-1} d.m. (Fig. 1).

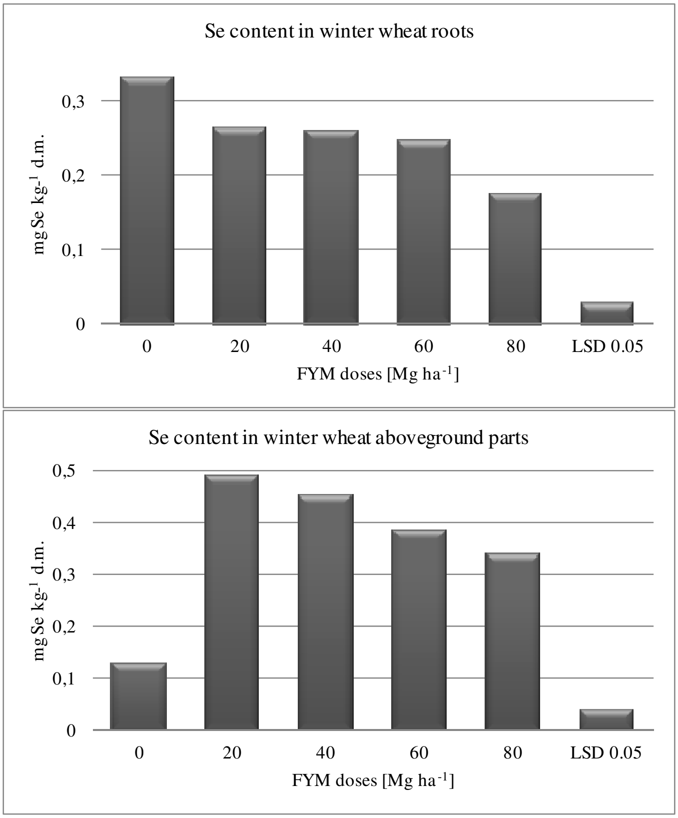

Fig. 1. Selenium content in winter wheat aboveground parts and roots

There were observed the highest selenium concentrations in aboveground parts of winter wheat from the plots treated with the doses of 20 and 40 Mg · ha^{-1}, the Se content increased on average above 70% against the control. The application of manure in the doses of 60 or 80 Mg · ha^{-1} resulted in the decrease in selenium content in aboveground biomass of winter wheat. The selenium content in winter wheat roots from the control plots was on average above 30% higher than from the FYM plots (Fig. 1). The distribution of selenium in various parts of the plant differs according to the species, its phase of development and its physiological conditions. In Se-accumulators, Se is accumulated in young leaves during the early vegetative stage of growth, however at the reproductive stage, high levels of selenium were found in seeds, while the Se content in leaves is reduced [13]. The selenium concentration in grain and roots of cereal plants is often the same level, with lower amounts in the stems and leaves. Zayed et al [14] report on the distribution of selenium in plants also depending on the form and the concentration of selenium supplies to the roots and on the nature and concentration of other ions, especially sulphates and on the degree of Se fixation in soils. Plants absorb Se easily from alkaline soils, where it often exists in water-soluble forms. Although acid soils may contain high selenium concentrations, plants assimilate only small amounts since Se is bound by insoluble iron compounds or by organic matter of soil [11].

Conclusions

1. There was found a significant effect of FYM application on the total selenium content in the soil investigated. A supplement of manure at the dose of 80 Mg · ha^{-1} resulted in the significantly highest increase in total selenium content (almost 50%) in soil, as compared with the control soil. The total selenium content in soil was significantly correlated with the organic carbon content.
2. There were observed the highest selenium concentrations in the upper parts of winter wheat from the plots treated with FYM with the doses of 20 and 40 Mg · ha^{-1}, namely about 70% higher in comparison with the control plants. The FYM application in the dose of 80 Mg · ha^{-1} resulted in a decrease in the selenium content in aboveground parts of wheat.

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AKUMULACJA SELENU PRZEZ PSZENICĘ OZIMĄ (*Triticum aestivum* L.) POD WPŁYWEM WIELOLETNIEGO NAWOŻENIA NAWOZEM NATURALNYM

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Abstrakt: Celem przeprowadzonych badań było określenie zawartości selenu w glebie oraz jego akumulacji i rozmieszczenia w roślinach pszenicy ozimej po wieloletniej aplikacji nawozu naturalnego. Aplikacja obornika istotnie wpływała na zawartość selenu ogółem w badanej glebie, a zastosowanie nawozu naturalnego na poziomie 80 Mg · ha^{-1} zwiększyło zawartość tego mikroelementu o prawie 50% w odniesieniu do jego zawartości w glebie z obiektu kontrolnego. Zawartość selenu ogółem w glebie była dodatnio skorelowana z zawartością węgla organicznego. Najwyższą zawartość selenu w nadziemnych częściach pszenicy ozimej wykazano na obiektach, na których obornik stosowano w dawce 20 i 40 Mg · ha^{-1}, w porównaniu z roślinami kontrolnymi. Po zastosowaniu obornika w tych dawkach zawartość selenu wzrosła o ponad 70%. Aplikacja obornika w dawce 80 Mg · ha^{-1} spowodowała natomiast istotne zmniejszenie zawartości tego pierwiastka w częściach nadziemnych pszenicy.

Słowa kluczowe: selen, gleba, pszenica ozima, obornik

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NUMERICAL MODELING IN QUANTITATIVE AND QUALITATIVE ANALYSIS OF STORM SEWAGE SYSTEM OPERATIONAL CONDITIONS

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

Abstract: Exploitation of urban storm-water systems, affected by increased size of drainaged catchment, high variability of rainfall events, changes in relative surface sealing as well as increased usage of road transport vehicles resulting in changes of sewage flow and pollutants concentrations as well as loads entering the sewage receiver, seems to be the challenging engineering problem. Thus, the application of numerical modeling to multi-variant analyses of storm-water sewer systems operation and its influence on the natural environment becomes a standard procedure nowadays. This paper presents the attempt of numerical modeling application to quantitative and qualitative analysis of storm-water sewer system in conditions of the selected urbanized catchment in the town of population reaching 40 000. The US EPA's (United States Environmental Protection Agency) software SWMM 5 was applied to our studies. Three different rainfall events of various intensity and time were studied in our research. The presented analysis was based on sewage flow velocity, wastewater level along the pipelines and the load of pollutants leaving the sewer system. The sewage flooding from several join or inspection chambers was observed. Our studies reveal also the fact that the studied system is partially undersized. According to the lack of model calibration our observations should be treated as preliminary studies.

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

Exploitation of the municipal storm water systems, in accordance to variable rainfall events, extension of urbanized area, changes in sealing of drainage surfaces and increased usage of transportation vehicles is a challenging engineering task, may result in variable hydraulic conditions of sewage flow and pollutants concentrations and loads entering the sewage receiver. Moreover, periodical water gathering in join and inspection manholes and even flooding may appear. Appearance of periodical flooding should be certainly treated as disadvantageous phenomena, seriously affecting the everyday life of municipal settlement. Increase of concentrations and loads of pollutants transported by storm sewage may negatively influence the quality of water in the wastewater receiver [1-4]. Thus, taking the above into consideration one may state that operation of the municipal storm water system seems to be a challenging engineering problem.

Storm wastewater, as it was frequently reported in literature, in dependence to type and manner of drainaged urbanized basin usage contain significant concentrations of pollutants *eg*: total suspended solids (TSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen (TN), total phosphorus (TP), heavy metals and oil derivatives [5-7]. Considering the above, in many European countries, according to European Water Frame Directive [8], the application of storm water drainage is being

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limited in favor of solutions based on collection and treatment of storm sewage in location of their generation [9, 10]. Hence, the analysis of increased discharge of storm sewage effect on receiver's water quality conducted at the stage of storm water network extension designing seems to be requisitive.

Management of the complex storm water systems for different rainfall events and various possible manners of network development for basins of different degree of sealing may be supported by numerical modeling. One of the most popular models applied in multivariate calculations is SWMM 5 (*Storm Water Management Model*) by United States Environmental Protection Agency (*US EPA*). This model allows dynamic quantitative and qualitative calculations of storm water network operation - the quality of offered calculations were repeatedly positively verified [4, 11, 12].

Presented studies focused on quantitative and qualitative analysis of storm water sewer system operation for the city of Swidnik, Poland. Our researches were based on numerical calculations conducted by SWMM 5. Flow velocity of storm wastewater, canals filling height as well as concentrations and loads of TSS at discharge location were selected as factors of our analyses.

Materials and methods

The modeled basin of area 2.47 km^2 covered the municipal system of storm water drainage the town of Swidnik, Poland. The total length of storm water system reached the value of approx. 48 km constructed of concrete pipes of diameters from DN 200 to DN 1600. Storm wastewaters are delivered to melioration drainage ditch and then to the Stawek-Stoki river.

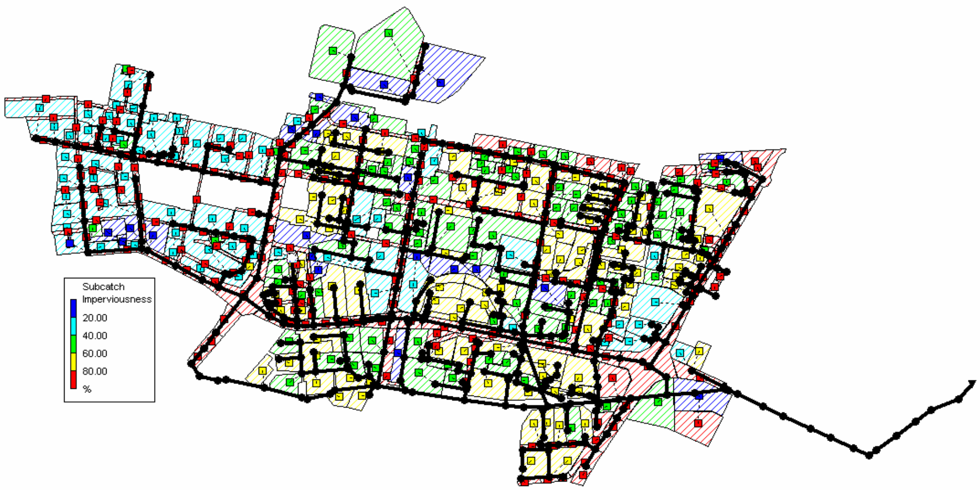

Fig. 1. Scheme of modeled basin

Numerical calculations of studied storm water network were conducted by SWMM 5 [13]. The numerical model of existing network, based on documentation accessed by system operator, is consisting of 500 subcatchments, 473 nodes, 476 lines and sewage receiver. Geometrical characteristics of the existing system and hydraulic parameters of pipes were read from the map and selected from SWMM 5 documentation [14]. The developed model was presented in Figure 1.

Our numerical calculations were conducted for three different rainfall events (various intensity and duration of rain). Parameters of applied rainfall events, were obtained from the local weather station in Felin, district of Lublin, Poland, approx. 3.0 km from the Swidnik city limits.

Unit runoff for rain No. I of duration t = 15 h was accepted as 2.67 $dm^3 \cdot s^{-1} \cdot ha^{-1}$, rainfall event No. II t = 15 h 4.33 $dm^3 \cdot s^{-1} \cdot ha^{-1}$, and event No. III t = 4 h 18.47 $dm^3 \cdot s^{-1} \cdot ha^{-1}$. The precise information about rainfall events assumed to modeling are presented in Table 1 while its time-varied distribution is shown in Figure 1.

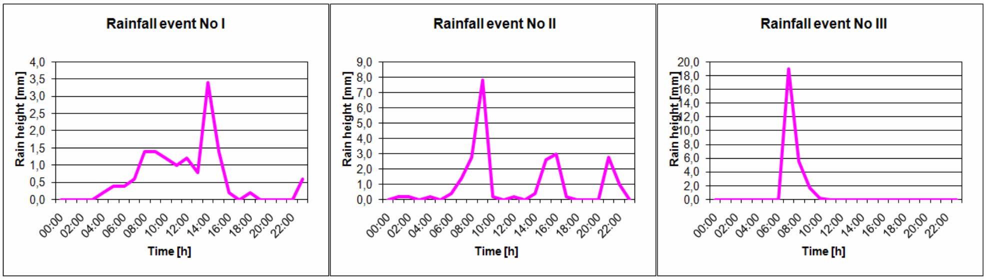

Fig. 2. Time dependant intensity of rainfall events applied to modeling

Table 1

Characteristics of applied rainfall events

	Rain No. I	Rain No. II	Rain No. III
Rainfall event time duration [h]	15	15	4
Total rainfall height [mm]	14.40	23.40	26.60
Mean rainfall intensity [$mm \cdot h^{-1}$]	0.96	1.56	6.65
Unit runoff [$dm^3 \cdot s^{-1} \cdot ha^{-1}$]	2.67	4.33	18.47

Qualitative numerical calculations were based on implemented in SWMM 5 equations of pollutants buildup and washoff on the catchment surface. The exponential model of pollutant buildup and *event mean concentration* (EMC) model of pollutant washoff were accepted [13, 14]. Input data were applied according to literature studies for two various types of land use (residential and undeveloped) distinguished in studied catchment [5, 15, 16].

Event mean concentration is a flow-weighted average value of selected pollutant concentration. Definition of EMC may be described as follows [17]:

$$EMC = \frac{\sum C_i Q_i}{\sum Q_i}$$

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

Input data for TSS (Table 2), TP and TN modeling were also based on literature studies [5, 15, 18-22].

Developed numerical model of storm water network in Swidnik, Poland requires empirical calibration based on multiple *in situ* measurements of qualitative and quantitative characteristics of studied system.

Table 2

Models and input data applied to TSS modeling

		Pollutant buildup	**Pollutant washoff**
Model of TSS		$B = C_1(1 - e^{C_2 t})$ B - pollutant buildup [mg · dm^{-3}] C_1 - maximum buildup possible [mg · dm^{-3}] C_2 - buildup rate constant [d^{-1}] t - time [d]	$W = C_2 \cdot Q^{C_3}$ W - concentration of pollutant in surface runoff C_3 - washoff coefficient, equal to EMC [-] C_4 - exponent, $C_4 = 1$ [-] Q - surface runoff flow rate [dm^3 · s^{-1}]
Applied values for TSS modeling	Residential area	$C_1 = 50$ mg · dm^{-3} $C_2 = 3$ d^{-1}	$EMC = 119.5$ [-]
	Undeveloped area	$C_1 = 100$ mg · dm^{-3} $C_2 = 3$ d^{-1}	$EMC = 206.5$ [-]
	Transportation area	$C_1 = 70$ mg · m^2 $C_2 = 0.3$ d^{-1}	$EMC = 89$ [-]

Results and discussion

The results of our calculations were presented in Figures 2-3 and in Table 3. Our calculations showed that for all cases studies, the velocity enabling self-purification of pipelines is achieved the significant share of pipes - from approx. 60% for the rain No. I to the nearly 80% for the most intensive rainfall No. III. However, the extensive flooding from 40 chambers was noted in case of rain No. III. Flooding for the others applied rainfall events was not so onerous, it appeared only in one and three chambers for rain No. I and No. II, respectively.

Table 3

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

	Unit	**Rain No. I**	**Rain No. II**	**Rain No. III**
Flow velocity [m · s^{-1}] < 0.3	[%]	16.60	11.14	6.30
Flow velocity [m · s^{-1}] > 0.6	[%]	59.66	77.31	78.99
Number of chambers endangered by flooding	[-]	1	3	40
TSS max concentration	[mg · dm^{-3}]	142.16	149.98	128.18

Results of our qualitative calculations showed that, maximum observed TSS concentration, reaching the value close to 150 mg · dm^{-3} exceeds the values allowable by Polish standards [23]. The graphical presentation of time dependant changes of TSS loads is shown in Figure 3. It's clearly visible, that time-varying loads of TSS reflect, to some extent, the shape of rainfall events intensity curves. Changes in shape are caused by the time delay from the moment in which rain achieves drainages surfaces, enters storm water network and finally, reaches its outflow.

The calculated TSS maximum concentrations for all applied rainfall events are in good agreement with values presented in literature reports [5, 17, 20, 21, 24], including EMC (Event Mean Concentration) values for various low and medium density urban catchments compiled by Park et al [12].

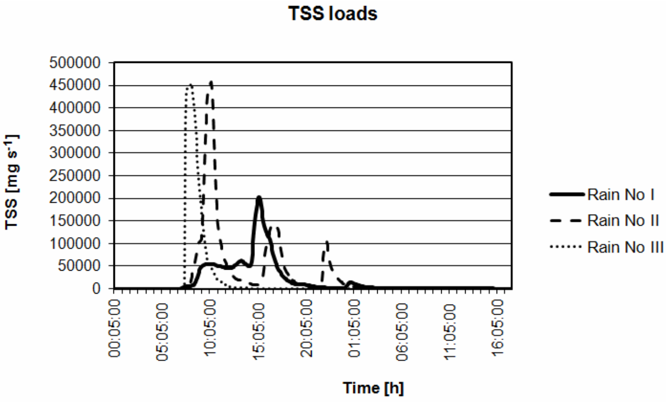

Fig. 3. Time-varying TSS loads leaving the modeled system

Summary

Our studies proved suitability of numerical modeling application to quantitative and qualitative analysis of storm water network development in conditions of Swidnik city, Poland. The obtained results show the satisfactory hydraulic conditions of storm wastewater flow in majority of pipelines for every tested rainfall. But we observed also the insufficient capability of the modeled network in sewage disposal for the rain of the highest intensity. As the result, the intensive flooding significantly disturbing the life of urbanized community was observed. The excess of acceptable load of tested pollutant in storm water discharged to the receiver was observed.

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

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

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Abstrakt: Przedstawiono próbę zastosowania modelowania numerycznego do ilościowej i jakościowej oceny możliwości rozbudowy systemu kanalizacji deszczowej. Model wybranego fragmentu sieci kanalizacyjnej miasta Chełm wykonano w programie SWMM 5. W badaniach przeanalizowano trzy warianty charakteryzujące się różną intensywnością oraz czasem trwania opadu. Obliczenia hydrauliczne wykonano dla warunków przed i po rozbudowie sieci. Przedstawiona analiza została oparta na prędkościach przepływu ścieków, napełnieniu kanałów oraz stężeniach i ładunkach transportowanych zanieczyszczeń. Po wykonaniu obliczeń symulacyjnych sieci po jej rozbudowie otrzymano wyniki, w których zaobserwowano zmiany w prędkości przepływu, napełnieniach kanałów, ładunkach badanego zanieczyszczenia. Odnotowano także w wynikach symulacji wypływ ścieków ze studzienek połączeniowych lub rewizyjnych na powierzchnię odwadnianego terenu. Przeprowadzone badania wskazują również, iż istniejący system zaprojektowany na podstawie wzoru Błaszczyka w obecnych warunkach jest częściowo przewymiarowany. W związku z tym prędkość samooczyszczania przewodów nie została osiągnięta w znacznej części sieci. Ze względu na brak kalibracji modelu otrzymane wyniki należy traktować jako wyniki badań wstępnych.

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

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KINETICS OF DEGRADATION OF MINERAL OIL AND DIESEL FUEL IN SOIL CONTAMINATED WITH PETROLEUM SUBSTANCES AFTER STIMULATION WITH FYRE-ZYME ENZYME REAGENT AND HYDROGEN PEROXIDE

KINETYKA ROZKŁADU OLEJU MINERALNEGO I NAPĘDOWEGO W GLEBIE SKAŻONEJ SUBSTANCJAMI ROPOPOCHODNYMI PO STYMULACJI PREPARATEM ENZYMATYCZNYM FYRE-ZYME I NADTLENKIEM WODORU

Abstract: Petroleum substances are widely used in many industries and are used as lubricants and fuels in motor vehicles. Due to the pipeline failure, lost of substances on the loading stations area and traffic crashes, petroleum contamination of soils are very common. High concentration of petroleum pollutants in the soil, leads to reduced activity of the indigenous microflora and extends their fate in the environment. The high costs of removal of oil spills to the soil and ground, forces to search for low-cost and effective methods of soils decontamination by „in situ" methods. The aim of this study was to compare the effectiveness of biodegradation of diesel fuel and mineral oil in the soil contaminated with petroleum substances, after "Fyre-Zyme" enzyme reagent stimulation and/or hydrogen peroxide. Obtained results indicate on stimulation of degradation process of diesel fuel and mineral oil, either by used enzyme and hydrogen peroxide compared with the control samples in 60 days period. This indicates the possibility of use of tested additives for soils bioremediation processes.

Keywords: oil, bioremediation, soil, enzymes, hydrogen peroxide

Petroleum substances are widely used in many industries and are used as lubricants and fuels in motor vehicles. Due to the pipeline failure, lost of substances on the loading stations area and traffic crashes, petroleum contamination of soils are very common. High concentration of petroleum pollutants in the soil, leads to reduced activity of the indigenous microflora and extends their fate in the environment [1-3]. In case of low amount of hydrocarbons contamination, it is possible use of compost and lime for improve natural degradation processes and plants growth conditions [4]. But high load of diesel fuel or lubricants lead to very long time of natural bioremediation. The high costs of removal of oil spills to the soil and ground, forces to search for low-cost and effective methods of soils decontamination by "in situ" methods [3, 5, 6].

The aim of this study was to compare the effectiveness of biodegradation of diesel fuel and mineral oil in the soil heavily contaminated with petroleum substances, after "Fyre-Zyme" enzyme reagent stimulation and/or hydrogen peroxide.

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Material and methods

Determination of the degree of degradation of diesel fuel and mineral oil in contaminated soil was conducted in the laboratory conditions by use:

- enzyme preparation Fyre-Zyme (S + FZ)
- hydrogen peroxide (S + H)
- preparation Fyre-Zyme enzyme and hydrogen peroxide (S + FZ + H)

Each experimental pot was fed by 1 kg of contaminated soil, and then the enzyme reagent Fyre-Zyme was added in an amount of 10% (m/m). Hydrogen peroxide was added in an amount of 0.5 g O_2/dm^3. Control samples (C) without the addition was incubated. Humidity was maintained at 60% and at 2 days periods weight loss of water was replenished. The prepared soil in pots were incubated at room temperature 22 (±2°C). The duration of the experiment was 60 days. Pot experiments established in 3 replications.

The kinetics of the chemical changes were monitored by taking 1 g soil samples from each pots, and then averaged and at 0, 30 and 60 days was determined changes in the concentration of oil products (diesel fuel and mineral oil) in the soil. Also only aliphatic hydrocarbons were determined. These compounds were divided on two group (C8-C21 and C22-C40) connected to boiling temperatures characteristic for diesel and mineral oil.

Aliphatic hydrocarbons, diesel fuel and mineral oil were determined by GC-FID method on capillary column VF1-ms (30 m x 0.53 mm x 1.50 μm). All samples were extracted in fexIKA extractor after drying with anhydrous sodium sulphate [7]. Diesel fuel and mineral oil were calculated as summary peaks of all detected organic compounds in specific boiling temperature ranges.

Results and discussion

Obtained results indicate on stimulation effect of used additions on petroleum products in investigated soil. On the end of experiment (60 day indicated by grey bars in Fig. 1) diesel fuel concentration was lower in all tested samples. The highest effectivity was noted in pot with hydrogen peroxide addition (S + H). Over 44.1% of diesel fuel was degraded in 60 days period (Fig. 1). Also in control sample degradation process was effective (29.8% of decomposition). Similar situation was noted in degradation of mineral oil. Best results were obtained in case of S + H sample (43.9%). Biodegradation results in case of stimulation with Fyre Zyme reagent with or without hydrogen peroxide was equal (37.8% in both samples). Worst results were obtained in control sample - only 21.7% (Fig. 2). This shows that long-chain hydrocarbons are more resistant on microbial degradation than compounds with short carbon chain.

Degradation of n-alkanes was different in all tested samples. In case of “short-chain” compounds, the best results were obtained in sample with hydrogen peroxide addition 54.0% (similar to total diesel fuel content). Worst results for these compounds (only 18.1%) were observed in samples with enzyme reagent. In case of “long-chain” n-alkanes (C22-C40), the highest degradation intensity (46.5%) was observed in samples with enzymes and with enzyme Fyre-Zyme. Similar to diesel fuel in samples with enzymes and H_2O_2 addition and only with hydrogen peroxide was observed good results (41.2 and 40.3% respectively) (Figs. 3 and 4).

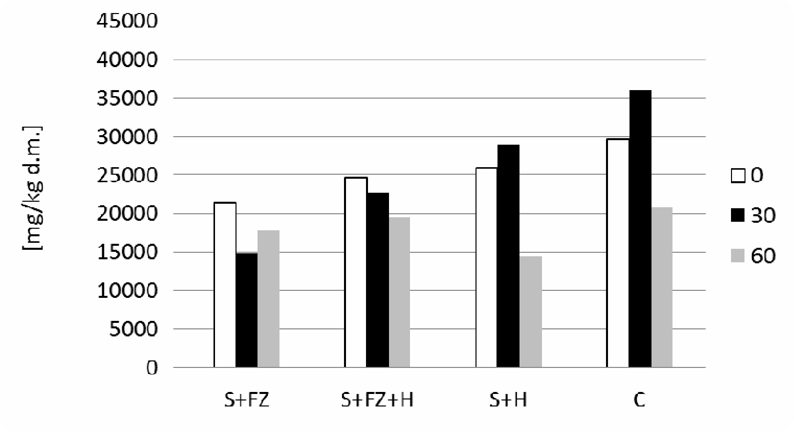

Fig. 1. Diesel fuel content in soil samples with different additions

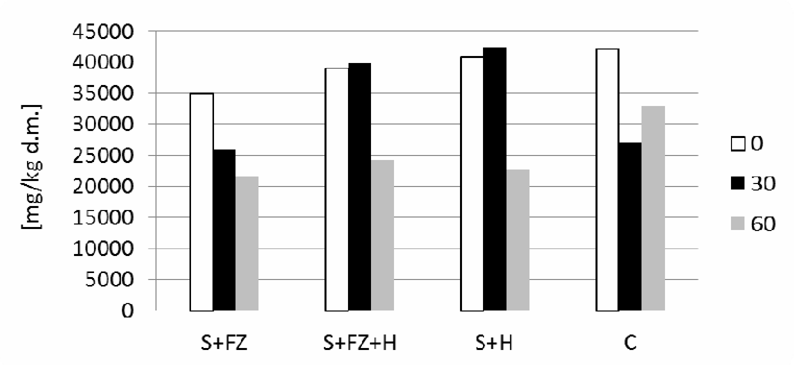

Fig. 2. Mineral oil content in soil samples with different additions

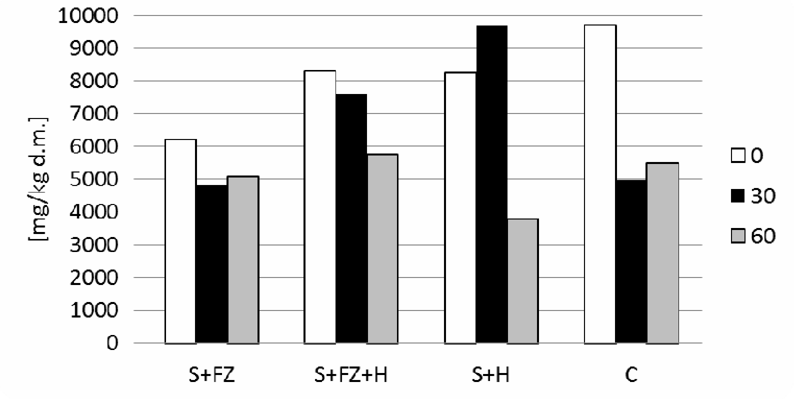

Fig. 3. Aliphatic hydrocarbons (C-8-C21) content in soil samples with different additions

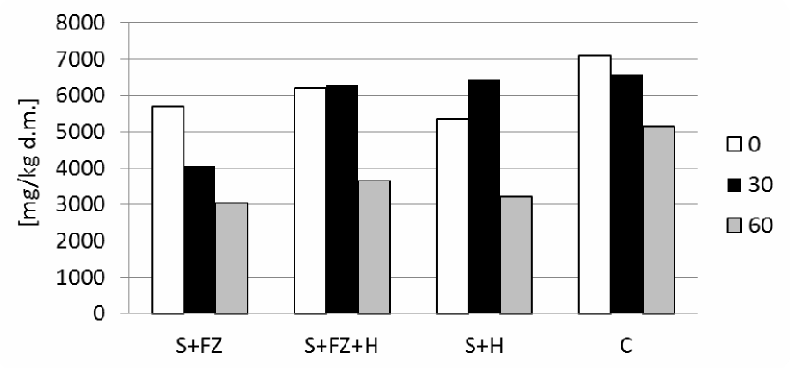

Fig. 4. Aliphatic hydrocarbons (C-22-C40) content in soil samples with different additions

Conclusion

Obtained results indicate on stimulation of degradation process of diesel fuel and mineral oil in heavily contaminated soil. The best results were obtained either for samples with Fyre-Zyme enzyme or hydrogen peroxide compared with the control samples in 60 days period. Compilation of enzyme reagent and hydrogen peroxide also was effective but especially for heavy compounds (*eg* mineral oil fraction). This indicates the possibility of use of tested additives for environmentally friendly, highly effective soils bioremediation processes.

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KINETYKA ROZKŁADU OLEJU MINERALNEGO I NAPĘDOWEGO W GLEBIE SKAŻONEJ SUBSTANCJAMI ROPOPOCHODNYMI PO STYMULACJI PREPARATEM ENZYMATYCZNYM FYRE-ZYME I NADTLENKIEM WODORU

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Abstrakt: Substancje ropopochodne znajdują szerokie zastosowanie w wielu gałęziach przemysłu, a także są stosowane jako środki smarne i pędne w pojazdach mechanicznych. Z uwagi na awarie sieci przesyłowych, obrót tymi substancjami na stacjach przeładunkowych, a także katastrofy w ruchu lądowym zanieczyszczenia ropopochodne gleb są częstym zjawiskiem. Duża koncentracja zanieczyszczeń naftopochodnych w glebie prowadzi do zmniejszenia aktywności mikroflory autochtonicznej i wydłuża czas ich zalegania w środowisku. Wysokie koszty likwidacji skutków wycieków ropopochodnych do gleb i gruntu zmuszają do poszukiwania tanich i efektywnych metod usuwania zanieczyszczeń metodami „in situ". W pracy porównano efektywności biodegradacji oleju napędowego i mineralnego w glebie skażonej substancjami ropopochodnymi po stymulacji preparatem enzymatycznym Fyre-Zyme lub/i nadtlenkiem wodoru. Zastosowane preparat enzymatyczny oraz nadtlenek wodoru stymulują rozkład oleju napędowego oraz mineralnego w glebie w porównaniu do grupy kontrolnej w okresie 60 dni. Wskazuje to na potencjalne możliwości zastosowania badanych dodatków do bioremediacji gleb.

Słowa kluczowe: ropopochodne, bioremediacja, gleba, enzymy, nadtlenek wodoru

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ESTIMATION OF RADIOACTIVITY DOSE RATE ABSORBED WITH INGESTED MUSHROOMS AND RELATED HEALTH RISK

OCENA DAWKI WCHŁANIANEJ W WYNIKU SPOŻYCIA GRZYBÓW I RYZYKO DLA ZDROWIA Z TYM ZWIĄZANE

Abstract: The fruiting bodies of fungi sprout from mycelium are capable of accumulating significant amounts of trace elements, both metals and metalloids. Content of these elements in fruiting bodies may exceed their concentration in the substrate where fungi develop. Among the elements the radioactive nuclides are also present. In this work health risk caused by increased radioactivity dose absorbed with *Xerocomus badius* bay bolete consumption was estimated. In analysis concentrations of radioactive isotopes ^{137}Cs and ^{40}K were taken into consideration. It was found that moderate ingestion of bay bolete does not create health risk due to increased radioactive substances intake. The amount of consumed mushrooms that could deliver the dose exceeding the safe one, is rather improbable in real life.

Keywords: fungi, isotopes, radioactivity dose

Mushrooms can accumulate heavy metals in general, including radionuclides found in the nature. Radionuclides present in the environment are absorbed both from soil through mycelium, and directly through the whole fruiting body surface [1]. The examination of ^{137}Cs content in fungi demonstrated significant selectivity in absorbing this radionuclide from soil. The following species demonstrated the highest level of caesium absorption: poisonous (though sometimes consumed) brown roll-rim (*Paxillus involutus*), as well as the tasty and popular bay bolete (*Xerocomus badius*) [2-6]. The mechanism of absorbing caesium by bay bolete was explained by the presence in its fruiting body cap of phenyl dye (the so-called badion A), which complexes potassium ions and alternatively caesium ions [7]. To evaluate the radiological impact we calculated the dose due to mushroom consumption. This parameter is primarily conditioned by the radionuclide concentrations in the mushrooms.

Materials and methods

The samples of bay bolete were collected in three areas:

A - forests in the Hradce Kralove area,
B - forests near Trebechovice pod Orebem,
C - forests of Kotlina Klodzka, the border zone between Poland and Czech Republic.

The measurement of ^{137}Cs and ^{40}K activity in mushrooms were carried out by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution: 1.29 keV (FWHM) at 662 keV and 1.70 keV (FWHM) at 1332 keV. Relative efficiency: 21.7%. Energy and efficiency calibration of the gamma spectrometer was performed with

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the standard solutions type MBSS 2 (Czech Metrological Institute, Prague, CZ) which covers an energy range from 59.54 to 1836.06 keV. Geometry of calibration source was Marinelli (447.7 ± 4.48 cm^3) with density 0.985 ± 0.01 g/cm^3, containing ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, ^{88}Y and ^{203} Hg. Geometry of samples container was Marinelli, 450 cm^3. Measuring process and analysis of spectra were computer controlled with use of the software GENIE 2000. The radiation spectrum was recorded day and night.

Results and discussions

The obtained measurement results, as well as the information published in relevant legal acts binding in Poland, were used for the assessment of risk related to the consumption of bay bolete. The indicators included in the Regulation [8] were applied in order to calculate the annual dose of internal exposure, caused by the consumption of bay bolete collected in the examined area. The loading effective dose *E*, being a result of a nuclide penetrating through the digestive system, was calculated from the formula:

$$E = e(g)A \tag{1}$$

where *e*(*g*) is conversion factor for persons in the age group *g* expressed in [Sv/Bq], and *A* is the activity of a radionuclide, which penetrated into the organism through the digestive and respiratory systems, expressed in [Bq].

Together with the consumed fungus, our organism is penetrated not only by the natural radioactive isotopes (especially ^{40}K), but also by the radioactive ^{137}Cs, which is accumulated in all soft tissues, and consequently removed from the organism.

The committed effective doses of ^{137}Cs and ^{40}K, included in Table 4 of the Regulation for the total population, related to the penetration of a nuclide with the activity concentration of 1 Bq, are shown in Table 1.

It can be noticed that with the same level of nuclide activity penetrating the organisms of a child and adult, the child will receive a bigger dose. Due to the smaller total weight, the absorbed energy for one body weight unit will be higher for a child than for an adult.

Table 1

Values of the committed effective doses of ^{137}Cs and ^{40}K in different age groups *g*, related to penetration of a nuclide with the activity concentration of 1 Bq [30]

***e*(*g*) [Sv/Bq]**	***g* ≤ 1 year**	***g* > 1 year**	***g* = 2-7 years**	***g* = 7-12 years**	***g* = 12-17 years**	***g* >17 years**
^{137}Cs	$2.1 \cdot 10^{-8}$	$1.2 \cdot 10^{-8}$	$9.6 \cdot 10^{-9}$	$1.0 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$
^{40}K	$6.2 \cdot 10^{-8}$	$4.2 \cdot 10^{-8}$	$2.1 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$	$7.6 \cdot 10^{-9}$	$6.2 \cdot 10^{-9}$

Considering the fact that fungi are not an obligatory component of children's diet and are introduced only for older children, there were two age groups - 12-17 and above 17 - taken into account.

In order to calculate the committed effective dose *E*, resulting from the penetration of a nuclide through the digestive system (*ie* by the consumption of the examined fungi), it was assumed on the basis of EFSA data [9, 10] that the maximum fungus consumption in a longer period may reach the level of 100 g per week. This amount corresponds to the consumption of approximately 5 kg of fresh fungi per year and a higher level of consumption should only take place sporadically. Taking into consideration the fact that fresh fungi contain 90% of water, while dry fungi contain 15% of water, the adopted annual consumption level of dry fungi for further calculations of loading effective dose was determined at the level of 0.5 kg.

Table 2 presents data characterizing the distribution of committed effective dose as a result of the absorption of ^{137}Cs and ^{40}K together with the consumed fungus, for persons in a relevant age group. Minimum (*Min*) and maximum (*Max*) values, lower quartiles (Q_1), medians (Q_2), upper quartiles (Q_3), arithmetic mean values (*mean*) and standard deviation (*SD*) were presented.

Table 2

Distribution of committed effective dose as a result of ^{137}Cs and ^{40}K absorption together with the consumed fungus, for persons in a relevant age group

***E* [mSv/year]**	**Min**	**Max**	Q_1	Q_2	Q_3	**mean**	***SD***
	g = 12-17 years						
^{137}Cs	0.003	0.016	0.005	0.006	0.009	0.008	0.005
^{40}K	0.002	0.004	0.002	0.003	0.004	0.003	0.001
	$g \geq 17$ years						
^{137}Cs	0.003	0.016	0.005	0.006	0.009	0.008	0.005
^{40}K	0.001	0.004	0.002	0.002	0.003	0.002	0.001

The data included in the table indicate that the effective dose received together with the consumed fungus from ^{137}Cs is significantly higher than the dose from ^{40}K. Therefore, it can be ascertained that a diet rich in fungi may cause an increase of the received annual effective dose.

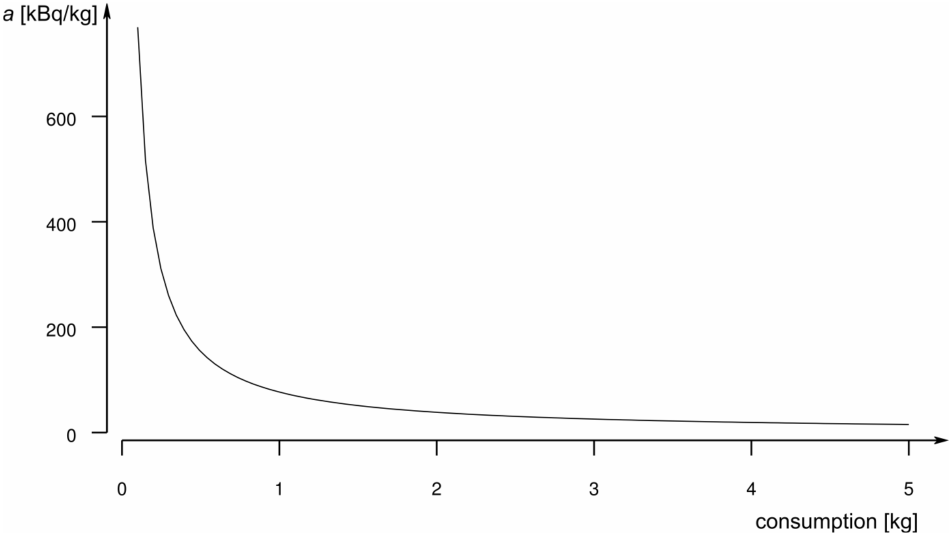

Fig. 1. The relationship between the consumption rate of bay boletes contaminated with ^{137}Cs and the level of this contamination, assuming that the dose of 1 mSv will not be exceeded (conversion factor $1.3 \cdot 10^{-8}$)

The analysis of data presented in the table allows to notice that the calculated maximum value of effective dose originating from ^{137}Cs amounts to 0.016 mSv/year, which is only 1.6% of the limit dose referred to in Regulations [8].

Figure 1 presents the relationship between the consumption rate of bay boletes contaminated with ^{137}Cs and the level of this contamination, assuming that the dose of 1 mSv will not be exceeded (for conversion factor $1.3 \cdot 10^{-8}$).

Assuming that a human being does not consume any other contaminated fungi or stay in a contaminated environment, the dose of 1 mSv will only be exceeded after consuming the amount of 0.25 kg of dried bay bolete with the activity of 300 kBq/kg. Also the consumption of 5 kg of dried fungi with the activity of approximately 15 kBq/kg will cause the dose of 1 mSv to be exceeded. Due to a small presence of fungi in the annual diet, as well as the maximum ^{137}Cs activity in dried bay bolete, amounting to approximately 1.2 kBq/kg, it can be acknowledged that the health risk related to the consumption of bay bolete collected in the examined area is insignificant.

Conclusions

Moderate ingestion of bay bolete collected in the investigated area does not create health risk due to increased radioactive substances intake. The amount of consumed mushrooms that could deliver the dose exceeding the safe one, is rather improbable in real life. The risk is also lowered because of obvious decrease of ^{137}Cs content in bay bolete.

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OCENA DAWKI WCHŁANIANEJ W WYNIKU SPOŻYCIA GRZYBÓW I RYZYKO DLA ZDROWIA Z TYM ZWIĄZANE

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Abstrakt: Owocniki grzybów wyrastające z grzybni są zdolne do gromadzenia znacznych ilości pierwiastków śladowych zarówno metali, jak i niemetali. Zawartość tych pierwiastków w owocnikach może wielokrotnie przekroczyć ich stężenia w podłożu. Wśród pochłoniętych pierwiastków są również nuklidy promieniotwórcze. Dokonano oceny potencjalnych dawek skutecznych promieniowania gamma w wyniku wchłonięcia ^{137}Cs i ^{40}K wraz ze spożywanym grzybem. Na podstawie wyników pomiarów stwierdzono, że umiarkowane spożycie podgrzybka brunatnego nie stwarza zagrożenia dla zdrowia ze względu na zwiększone spożycie substancji radioaktywnych.

Słowa kluczowe: grzyby, radionuklidy, metale alkaliczne

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DIFFERENTIAL SENSITIVITY OF THE *Lemnaceae* SPECIES TO CHROMIUM AND ZINC

WRAŻLIWOŚĆ RODZINY *Lemnaceae* NA CHROM I CYNK

Abstract: The aim of study was to optimize alternative acute toxicity tests involving toxic compounds of Cr(VI) and Zn(II) and two representatives of the *Lemnaceae* species (*Lemna gibba* and *Spirodela polyrhiza*) as testing organisms and to compare their relative sensitivity with *Lemna minor* and *Daphnia magna*. The most sensitive organism to both metals was *D. magna*. The highest duckweed sensitivity to Cr(VI) and Zn(II) was determined for *S. polyrhiza* and *L. gibba*, respectively. The compound of Cr(VI) provided significantly higher toxicity effect towards the testing organisms than Zn(II). *L. gibba* proved the most suitability for assessment of environmental quality due to the highest duckweed sensitivity. In contrast, *L. minor* and *S. polyrhiza* showed the lowest sensitivity to Cr(VI) and Zn(II), respectively. It was probably caused by their antioxidant ability, and thus they may be the most effective for removal of metals from water environment.

Keywords: ecotoxicological test, chromium, zinc, the *Lemnaceae* family, acute toxicity test, growth inhibition

An environmental pollution by various pollutants is a serious problem with harmful impacts on living organisms (*eg* gene mutation, cancer, influencing of growth, development, and reproduction) [1, 2]. Inorganic compounds containing arsenic, cadmium, chromium, copper, mercury, zinc, or lead that are easily accumulated in soil or living organisms are considered to be the most detrimental elements to the environment [2-4]. The aquatic plants from the *Lemnaceae* family are able to accumulate heavy metals [5, 6]. The danger is that they serve as feed for fish and waterfowl and thus may be a potential risk for humans [2]. On the other hand, they can help in removing excess of toxic metals from surface water [6-8]. The aim of study was to optimize alternative acute toxicity tests involving toxic compounds of Cr(VI) and Zn(II) and two *Lemnaceae* species (*Lemna gibba* and *Spirodela polyrhiza*) as testing organisms, and to compare their relative sensitivity with *Lemna minor* and *Daphnia magna*.

Experimental

All chemicals used were of analytical grade. Stock solutions and culture media were prepared according to the ISO 20079 [9] and ISO 6341 protocols [10]. Solutions of $K_2Cr_2O_7$ (200 mg/dm^3) and $ZnSO_4 \cdot 7H_2O$ (100 mg/ dm^3) were used as stock standards.

Alternative growth inhibition tests and the standard growth inhibition test with *L. minor* were performed according to the biotest based on the ISO 20079 protocol [9]. Tested duckweed culture media contained 0÷140, 0÷50, 0÷30 mg/cm^3 $K_2Cr_2O_7$, or 0÷30, 0÷10, and 0÷40 mg/cm^3 $ZnSO_4 \cdot 7H_2O$ for *L. minor*, *L. gibba*, and *S. polyrhiza,*

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respectively. Tested species of duckweeds were taken from billabong river Orlice. To the tests were chosen completely healthy duckweed plants with 2-4 fronds after laboratory recultivation. Total number of fronds in 100 cm^3 solutions was 20 or 10 for *L. minor* and *L. gibba*, or *S. polyrhiza*, respectively. All solutions were covered by transparent film and placed into thermostat at 24°C with permanent light. Status of plants and number of duckweed fronds were controlled for all tested concentrations during 14 days. Growth inhibition percentages (I) were calculated according to $I = (C - S)/C \cdot 100\%$, where C and S represent the number of live fronds in control and sample, respectively. The half maximal inhibitory concentrations (IC50), which mean 50% duckweed growth inhibition, were determined using regression equations from the dependences of growth inhibition on concentration of toxic compound.

The standard acute toxicity test with *Daphnia magna* was carried out according to the biotest based on the ISO 6341 protocol [10]. Tested daphnia cultivation media contained 0÷2 mg/cm^3 $K_2Cr_2O_7$ and 0÷10 mg/cm^3 $ZnSO_4 \cdot 7H_2O$. Only moving daphnids of age in 24 hours from prebreeding were used for the tests and their total number reached 10 in 100 cm^3 (max. 1 daphnia/5 cm^3). Death loss in control solution was lower than 10%. All solutions were placed into thermostat at 20°C with the ratio of light cycle 16 : 8 (light : darkness) without aeration and feed. Numbers of immobilized daphnids were determined after 24 and 48 hours for all tested concentrations. Mortality percentages (M) was calculated according to $M = (C - S)/C \cdot 100\%$, where C and S represent the number of immobilized daphnids in control and sample, respectively. The half maximal effective concentrations (EC50), which refer to 50% inhibition of their mobility, were determined using regression equations from the dependences of death loss on concentration of toxic compound.

Results and discussion

The presented study deals with the comparison of relative sensitivity of three aquatic plants from the *Lemnaceae* family to compounds comprising hexavalent chromium and bivalent zinc as potential toxic metals. Common duckweed (*L. minor*) is a worldwide species which is commercially used in ecotoxicological laboratories and research. Figure 1 shows the deleterious impact of zinc sulfate on the growth of *L. minor*. Fat duckweed (*L. gibba*) and greater duckweed (*S. polyrhiza*) were selected as representatives of duckweed species naturally occurring in Czech Republic and their potential sensitivity was compared with *L. minor* and *D. magna*.

Figure 2 displays the assessment of growth inhibition of *L. gibba* and *S. polyrhiza* induced by potassium dichromate and zinc sulfate. All determined IC50 and EC50 are stated in Table 1. Comparison of the relative sensitivity of three duckweed species, and *Daphnia magna* is presented in Figure 3. The chromium and zinc sensitivity decrease in the order: *D. magna* > *S. polyrhiza* > *L. gibba* > *L. minor* and *D. magna* > *L. gibba* > *L. minor* > *S. polyrhiza*, respectively.

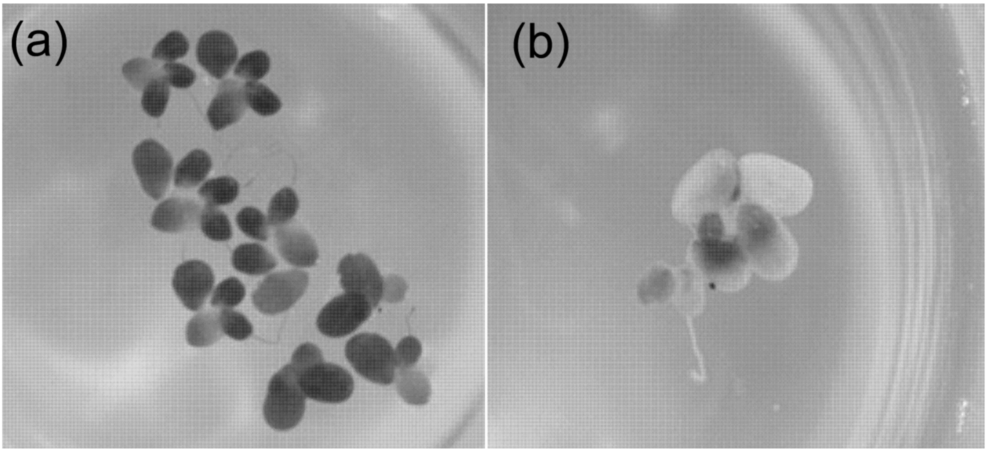

Fig. 1. Lesser duckweed (*Lemna minor*) in the absence (a) and presence (b) of $ZnSO_4 \cdot 7H_2O$ (10 mg/dm^3) after 14 days at 24°C

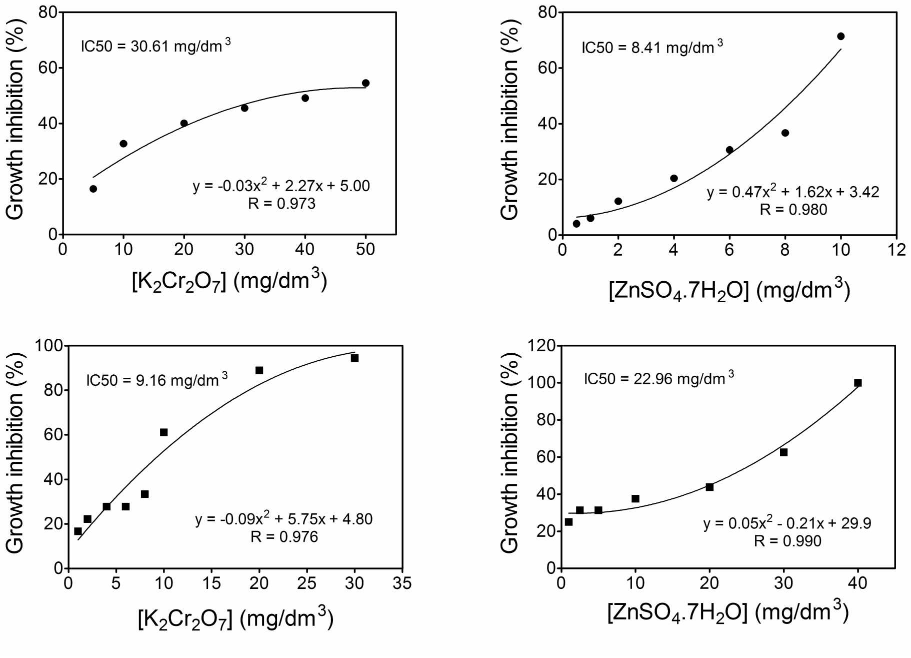

Fig. 2. Growth inhibition of *Lemna gibba* (●) and *Spirodela polyrhiza* (■) by $K_2Cr_2O_7$ and $ZnSO_4 \cdot 7H_2O$ solutions after 14 days at 24°C

The obtained results showed that the most sensitive organism to both studied compounds was aquatic arthropod *D. magna*. The highest duckweed sensitivity to Cr(VI) was determined for *S. polyrhiza*. It was more than six or nine times lower in the comparison with *D. magna* after 24 or 48 h, respectively. *L. gibba* showed more than three times and *L. minor* even seven times lower sensitivity to potassium dichromate than *S. polyrhiza*. The highest duckweed sensitivity to Zn(II) was noticed for *L. gibba*. Its IC50 value was close or half to the EC50 values of *D. magna* after 24 h or 48 h, respectively. *L. minor* showed a slightly lower and *S. polyrhiza* less than three times lower sensitivity to zinc sulfate than *L. gibba*. The compound of hexavalent chromium possessed significantly higher toxic impact towards the testing organisms. The obtained results showed that *L. gibba* is the most suitable duckweed for assessment of environmental quality due to its highest sensitivity towards the tested compounds.

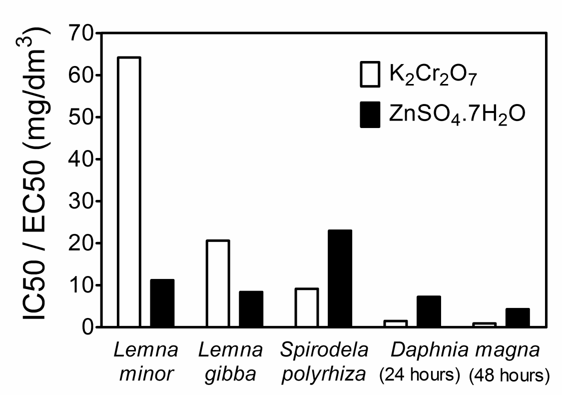

Fig. 3. Sensitivity of the tested *Lemnaceae* species and *Daphnia magna*

Table 1

Growth inhibition of the tested *Lemnaceae* species after 14 days and death loss of *Daphnia magna* caused by $ZnSO_4 \cdot 7H_2O$ and $K_2Cr_2O_7$

Organism	**IC50 [mg/dm^3]**			
	$K_2Cr_2O_7$	**$ZnSO_4 \cdot 7H_2O$**	**Cr^a**	**Zn^a**
Lemna minor	64.2	11.2	22.7	2.55
Lemna gibba	30.6	8.41	10.8	1.91
Spirodela polyrhiza	9.16	23.0	3.24	5.06
	EC50 [mg/dm^3]			
	$K_2Cr_2O_7$	**$ZnSO_4 \cdot 7H_2O$**	**Cr^a**	**Zn^a**
Daphnia magna (24 hours)	1.51	7.24	0.54	1.64
Daphnia magna (48 hours)	0.92	4.30	0.32	0.98

[a] Conversion to IC50 or EC50 related to toxic metal

Also Lahive et al [11] observed that *L. gibba* is more sensitive to zinc sulfate than *L. minor*. In contrast, no significant difference in sensitivity towards potassium dichromate between *L. minor* and *L. gibba* was noticed by Cowgill et al [12] and Henke et al [13] observed no obvious induction of frond abscission in *L. minor* caused by Cr(VI) and Zn(II). It was described that the *Lemnaceae* species are able to accumulate heavy metals and some organic pollutants [12, 14]. Consequently they can be involved in food chain and threatened living organisms including humans [2]. On the other hand, the duckweed species may be used for efficient elimination of toxic pollutants and thus may ultimately serve as phytoremediation agents in the natural environment [6-8, 14]. It was showed that *L. gibba* was able to remove metals such zinc, copper, or cadmium from the aqueous medium [8]. Our obtained data suggest that *L. minor* and *S. polyrhiza*, which showed the lowest chromium and zinc sensitivity, respectively, may be the most effective for removal of these metals from water environment. The decrease of duckweed sensitivity to toxic compounds is probably related to their antioxidant ability which saves the plants from cells damage caused by production of reactive oxygen species during the oxidative stress. Uruc-Parlak and Demirezen Yilmaz [15] proposed that *L. minor*, *L. gibba*, and *S. polyrhiza* are supplied with an efficient antioxidant mechanism against zinc induced oxidative stress. Radic et al [16] demonstrated that *L. minor* has a potential for phytoremediation of water bodies polluted by zinc and aluminum due to its high bioaccumulation potential and tolerance *via* increased antioxidant capacity.

Conclusions

The obtained results showed that the most sensitive organism to both studied compounds was *D. magna*. The hexavalent chromium provided significantly higher toxicity effect towards the testing plants than bivalent zinc. The highest sensitivity of duckweed species to Cr(VI) and Zn(II) was determined for *S. polyrhiza* and *L. gibba*, respectively. *L. gibba* proved the most suitability for assessment of environmental quality due to its highest sensitivity from the tested duckweeds. On the other hand, *L. minor* and *S. polyrhiza* showed the lowest sensitivity to Cr(VI) and Zn(II), respectively, and thus may be the most effective for removal these metals from water environment. It is probably related to their efficient antioxidant ability.

Acknowledgements

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WRAŻLIWOŚĆ RODZINY *Lemnaceae* NA CHROM I CYNK

Abstrakt: Celem pracy była optymalizacja alternatywnych testów ostrej toksyczności z udziałem toksycznych związków Cr(VI) i Zn(II) i dwóch przedstawicieli gatunku Lemnaceae (*Lemna gibba* i *Spirodela polyrhiza*) jako organizmów testowych i porównanie ich względnej czułości w stosunku do *Lemna minor* i *Daphnia magna*. Organizmem najbardziej wrażliwym na oba metale była *D. magna*. Największą wrażliwość na Cr(VI) i Zn(II) stwierdzono odpowiednio dla *L. gibba* i *S. polyrhiza*. Związek chromu(VI) powodował silniejszy efekt toksyczny w organizmach testowych niż Zn(II). Ze względu na najwyższą czułość *L. gibba* jest najlepszym biomonitorem do oceny jakości środowiska naturalnego. Najmniejszą wrażliwość na Cr(VI) i Zn(II) wykazały odpowiednio *L. minor* i *S. polyrhiza*. Jest to prawdopodobnie spowodowane ich zdolnościami antyoksydacyjnymi i dlatego mogą być one najbardziej skuteczne w usuwaniu metali ze środowiska wodnego.

Słowa kluczowe: badania ekotoksykologiczne, chrom, cynk, rodzina *Lemnaceae*, badanie ostrej toksyczności, zahamowanie wzrostu

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CHANGEABILITY MODEL OF THE BOG ORE HYDROGEN SULFIDE SORPTION ABILITY

MODEL ZMIENNOŚCI ZDOLNOŚCI SORPCYJNEJ RUDY DARNIOWEJ WZGLĘDEM SIARKOWODORU

Abstract: Basing on long-standing cyclic measurements of sludge-originated biogas composition and considering statistical analysis of their results, a regression model describing time variation of biogas desulfurization using bog iron ore has been developed. The model was verified by theoretical calculations and results from laboratory examinations of the sorbent. It was also used to estimate the depletion time and sorption capacity of the bed and to determine the demand index for bog ore.

Keywords: sewage sludge, fermentation, biogas, desulphurization, statistical analysis, forecasting

Having regard to the boom forecasted for biogas plants [1, 2], it would be necessary to develop biogas treatment methods, especially in the context of its industrial combustion. Removal of sulphur hydrogen, which creates threat for instrumentation and environment, is among one of the most important stages in biogas treatment process [3]. Due to availability of the sorbent and low related capital and operating costs, bog ore, the mineral including iron compounds reacting with H_2S, is commonly used for this purpose in Poland. However a barrier for its further effective use may be the lack of experimental data about its sorption capacity, mechanisms of sorption and the possibilities of its intensification.

The mathematical model of time variability of biogas desulfurization efficiency using bog ore was developed basing on long-standing, quarterly investigations of biogas generated from sludge in *Wroclaw Sewage Treatment Plant* (WSTP) [4]. It was then used to calculate the bed sorption capacity and to determine the sorbent demand index per 1,000 m^3 of biogas. The results from model calculations were compared with sorption capacity calculated theoretically and with the results of laboratory examinations.

This paper is continuation of the previous examinations [5]. Information about analytical methods is given in items [4-7] while that of generation and treatment of biogas under investigation - in [4, 8, 9].

Biogas desulphurization using bog ore

For the bog ore could be the H_2S sorbent, it shall be made free of minus 200 μm grain size fraction, organic substances and carbonate minerals. Activation of the ore consists in calcining, fluffing (*eg* by adding sawdust) and alkalizing with calcium hydroxide, sodium hydroxide or sodium carbonate [10].

Mechanism of biogas desulfurization using bog ore is strongly dependent on pH value. Alkaline medium is more favourable as it generates Fe_2S_3 which faster reacts with oxygen. This facilitates regeneration consisting in oxidizing ferrous sulpfide(III) back to the active

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form of ferrous oxide(III). In acid environment, the free sulphur coming out in a process, blocks the pores and faster deactivates active iron compounds.

Two parallel cylindrical desulfurization grid-type units with four filtration baskets are used for biogas desulfurization at Wroclaw Sewage Treatment Plant. The units are filled with bog ore from Strzyzow deposits near Kalisz, prepared according to the recipe of the Institute of Chemistry, Petroleum and Coal Technologies at Wroclaw University of Technology. Raw ore was modified by addition of alkaline activators (NaOH, Na_2CO_3) and fluffing agents in form of sawdust.

Statistical analyze

The model was developed on the basis of own 30 tests of the biogas desulfurization efficiency (η), made in the years 2002-2009, and dates of bed replacement. Investigations included two desulphurizers.

Three types of trends were examined: second degree polynomial $(\eta = 0.00225 \cdot \tau^2 - 0.726 \cdot \tau + 100)$, linear $(\eta = -0.374 \cdot \tau + 100)$ and exponential $(\eta = 100 \cdot \exp(-0.00682 \cdot \tau))$, to determine the H_2S removal efficiency versus sorption time (τ).

Reliability of regressions under analysis for describing time variability of desulfurization efficiency was evaluated using standard tools of statistical analysis (Table 1). For comparison purposes, the version of ideal relation between calculated and measured efficiencies was presented.

Table 1

Values of model estimation statistical indicators

Indicator	**Reference value** ($\eta_{oi} = \eta_{pi}$)	**Function**		
		Polynomial II deg.	**Linear**	**Exponential**
Correlation coefficient R	1	0.78	0.90	0.95
Deviation of averages D_C [%]	0	7.57	3.91	1.42
Relative deviation of averages W_C [%]	0	11.26	5.81	2.11
Average deviation B_C [%]	0	11.34	10.6	6.9
Relative average deviation O_C [%]	0	16.86	15.77	10.31

The dissipation diagram (Fig. 1) was made to evaluate the degree of overrating or underrating the results also. The points with coordinates (η_{pi}, η_{oi}) were introduced into the diagrams. Theoretical points should lie along a straight line inclined at 45° and starting from the origin of coordinate system. The degree of dispersion with respect of this line is the measure of model accuracy.

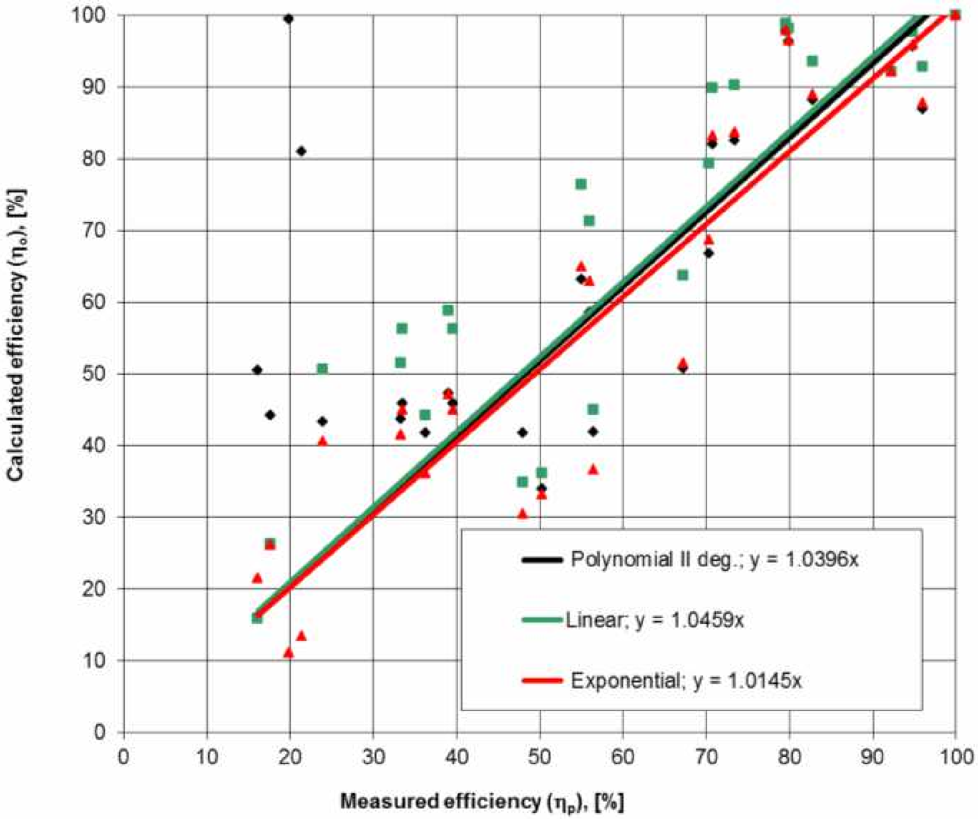

Fig. 1. Diagram of dissipation

Results and discussion

Upon analyzing the indexes of statistical evaluation for regression versions under consideration (Table 1) and the dissipation diagram (Fig. 1), the exponential model was selected for further calculations. It was used to find the trend lines of H_2S absorption efficiency decline with sorption time which lines were then included into particular measurement series (Fig. 2). Trend lines for particular measurement series put on measurement points show no essential dependence between the sorption capacity decline and absorbed load of H_2S. Hence, it appears that apart from hydrogen sulphide there are other factors which deactivate the ore. Potentially belongs to them: acidification of reaction environment by CO_2 (elementary sulphur, which precipitates under such conditions, blocks the pores and impedes H_2S access to active iron compounds [11]), oxygen existing in biogas, which causes that sulphides are oxidized to elementary sulphur [12], binding F^{3+} and Fe^{2+} iron by CO_2, leads to creating iron carbonates and bicarbonates which block the pores.

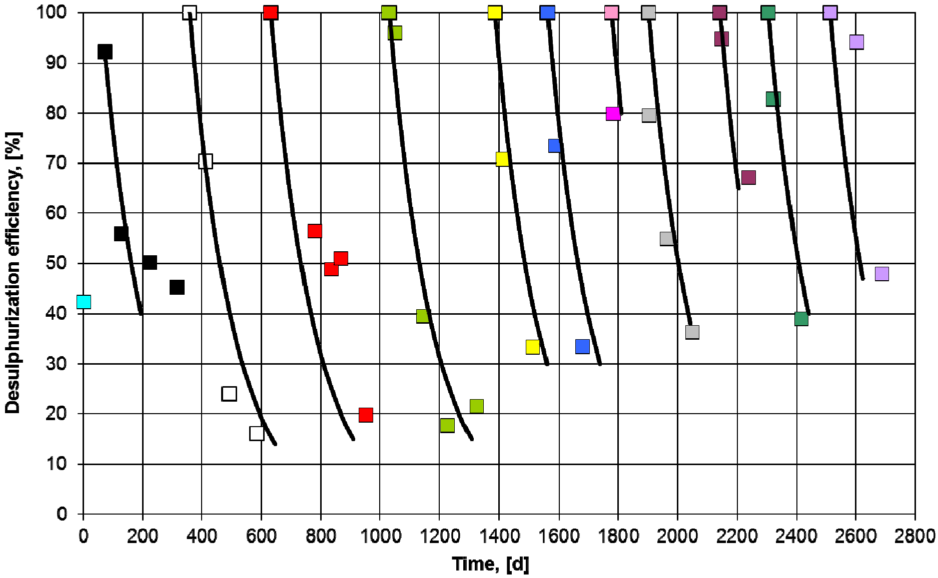

Fig. 2. Time changeability of H_2S removal efficiency

Verification and usage of the model

Model results of bed depletion time were compared with those from stoichiometric calculations and those from laboratory testing. The assumptions were that:

- the reaction of H_2S binding proceeds according to equations:

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O, \quad 2NaOH + H_2S \rightarrow Na_2SO_3 + 2H_2O$$

- concentration of H_2S in raw biogas, desulfurization efficiency, volumetric flow of biogas, volume and apparent density of the bed correspond to averaged values of these parameters for both desulfurization units over the full examination time (respectively: 153.7 mg/m_n^3, 54.5%, 219 m_n^3/h, 3.4 m^3 and 941 kg/m^3),
- bed humidity and content of Fe_2O_3 and NaOH in the bed are at averaged levels from laboratory testing (respectively: 50, 3.38, 22.91% d.m.).

In theory, considering exclusively the reactions with Fe_2O_3 (m_{H2S1}) and NaOH (m_{H2S2}), a single desulfurization unit can bind 258.4 kg H_2S. Hence, theoretical time of bed depletion, corresponding to average mass stream of absorbed H_2S equals 587 d.

According to laboratory results, the sorbent under consideration can absorb at least 0.1878 kg S/kg of bed dry matter, which corresponds to the time of complete exhaustion 725 d. But, according to the regression model proposed, while assuming the minimum final efficiency $\eta = 5\%$, the maximum time of total bed exhaustion can be evaluated at 439 d. Using the suggested model, it was also determined the expected efficiency of desulfurization units at the moment of bed replacement, which - as averaged for all measurement series - was c. 20%, practical (maximum) operating time of the bed (235 d) and practical absorbing power of bog ore (0.059 kg S/kg d.m.). On this grounds, the bog ore consumption index of purified biogas was estimated (0.0028 m^3/1000 m_n^3 of biogas).

Conclusions

Calculations made for statistical coefficients proved that the exponential model provides the best representation of time variability of bog ore sorption capacity for H_2S. The sorption capacity found from this model, corresponding to practical operating period of the bed, is 0.059 kg S/kg of dry matter which represents about 30% of the capacity attained in laboratory (the difference may result from difficulties in maintaining the optimum operating conditions, such as pH value, temperature and humidity, for desulfurization units under real conditions).

The demand index for bog ore evaluated by the model proposed is c. 0.003 $m^3/1000\ m_n^3$ of biogas, *ie* 2.6 $kg/1000\ m_n^3$.

For the technology of sewage treatment and biogas treatment under consideration, the total time of bed depletion calculated by the model developed is 439 days while practical period of bed operation (*ie* till the efficiency is 20%) - 235 days.

Sulphur hydrogen is neither the just one nor the most important factor of bog ore deactivation. It is the carbon dioxide contained in biogas which seems to be the main factor of sorption capacity decline. Also the sawdust added to fluff the bed and oxygen present in biogas have an adverse impact on chemical mechanisms of H_2S absorption.

Considering the good points of biogas desulfurization with bog ore (*ie* availability and low purchase costs of the sorbent, simple operation and high availability factor of the plant) and its drawbacks (relatively low and time-variable efficiency of H_2S removal, arduous replacement of the bed, problems with waste disposal, limited potential of process automation and control, lack of market-available product with uniform and standardized properties, *eg* granulate) and also the effects attained (in general, biogas meets, after desulphurization, the specifications demanded by gas motor manufacturers), a statement could be made that, under Polish conditions, biogas desulfurization with bog ore is justified mainly due to economical reasons. However, the method needs further studies. Many authors, like [13-15], draw attention to insufficient knowledge about sorption properties of bog ores and the sorption mechanisms as well.

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MODEL ZMIENNOŚCI ZDOLNOŚCI SORPCYJNEJ RUDY DARNIOWEJ WZGLĘDEM SIARKOWODORU

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Abstrakt: Na podstawie wieloletnich, cyklicznych pomiarów składu biogazu powstającego z osadów ściekowych, wykorzystując analizę statystyczną wyników, opracowano model regresyjny, opisujący czasowy charakter zmienności skuteczności odsiarczania biogazu za pomocą rudy darniowej. Model został zweryfikowany za pomocą obliczeń teoretycznych i wyników badań laboratoryjnych sorbentu. Za jego pomocą oszacowano czas wyczerpania i pojemność sorpcyjną złoża oraz wyznaczono wskaźnik zapotrzebowania na rudę darniową.

Słowa kluczowe: osad ściekowy, fermentacja, biogaz, odsiarczanie, analiza statystyczna, prognozowanie

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ECOLOGICAL RISK CLASSIFICATION IN THE REGULATED AND CONSERVED WATERCOURSES

KLASYFIKACJA RYZYKA EKOLOGICZNEGO W REGULOWANYCH I KONSERWOWANYCH CIEKACH

Abstract: The subject of the following study is ecological risk in regulatory and maintenance works conducted in small and medium-sized lowland watercourses. Risk has not been identified enough for the designers and contractors to take any actions for its limitation. The following research presents a proposal of solving the problem on an example of alternations in hydromacrophytes communities. The results of the field work conducted between 2007 and 2008 on 10 regulated, maintained and unmodified Lower Silesian lowland watercourses form a basis for this analysis. The research included hydromacrophytes identification and the degree of the bottom coverage by these aquatic plants. The analysis of quality and quantity alternations in aquatic plants communities concerning the range and conditions of works conduction enabled assigning measures to the factors of considered risk. It served as a basis for describing the matrix of risk classification. Three risk levels were accepted - low, moderate and high.

Keywords: aquatic vascular plants, ecological risk, maintenance works, watercourses regulation

In spite of knowledge base accessible in the matter of the impact of regulatory and conservation works on the water courses biocenosis there is no method allowing for biocenosis changes forecast being a result of technical works occurring in the river bed. The lack of such a tool results in the possibility of the assessment of the project after it has been done. Decisions taken by designers and contractors are assessed after the works completion. Taking into account that the effects of some decisions are irreversible for the environment it is crucial to take fast actions on solving the problem to assure environmental safety. The following research shows the proposal of using an assessment of ecological risk to cover the problem. The term "risk" defines a degree of exposure to harmful events and their possible consequences [1]. Determination of the level of ecological risk in regulated and conserved water courses serves a possibility of changes forecast in river beds ecosystems [2-4].

The aim of the following work is the determination of the principle to assess and classify ecological risk of regulatory and conservation works basing on one element of watercourse ecosystem - hydromacrophytes. These water plants are good bioindicators of the quality of water environment [5, 6]. Therefore, they are one of the basic factors considered in an assessment of the ecological state of flowing waters [7].

Study objects and methods

Field work was performed during vegetation periods in 2007 and 2008 in 10 small and medium Lower Silesian watercourses. These watercourses were divided into 34 experimental sections 100 meters long each. Experimental sections were located in similar climate, geological and soil conditions. Adjacent field was used agriculturally with

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a domination of arable lands and grasslands. Water in experimental sections was contaminated neither with urban or industrial wastes. Particular sections varied with the degree of anthropogenic transformation - 11 were located in the watercourses where conservatory works were done while other 13 were located in regulated watercourses. Each watercourse had one section where no works were conducted.

In the framework of the following field work macrophytes species was identified on the examined sections and the degree of the bottom coverage with them was determined. All hydromacrophytes rooted in water for at least 90% of the vegetation period and plants flowing naturally on the water surface or under it were taken into account. Five levels Braun-Blanquet scale was used for the determination of the density degree [8].

In order to assess species variety in the examined sections Shannon-Wiener index - *H* [9] was calculated. Risk level connected with conservation and regulatory works performance was defined according to the following formula [1]:

$$R = P \cdot S$$

In this formula: *P* - stands for the possibility of changes occurrence in the community of the hydromacrophytes in a result of works performance, *S* - stands for the size of these changes.

These factors were ascribed with different measurements. They were indicated by the field work results. In both cases 5 levels scales were used. Product of P and S parameters formed a basis of the risk level assessment. It was followed by two parametric matrix of the risk assessment [10]. According to accepted scales, matrix was marked due to observed changes in the plants community concerning works conducted in the examined watercourse.

Results

In the examined sections 20 species of aquatic macrophytes were determined altogether. According to Method of Macrophytes Rivers Assessment (MMOR) [11] these species have a wide or medium wide ecological scale and low or medium index value - *W* measured at 1 or 2. Figure 1 shows statistic data referring to aquatic plants occurrence in the examined river sections.

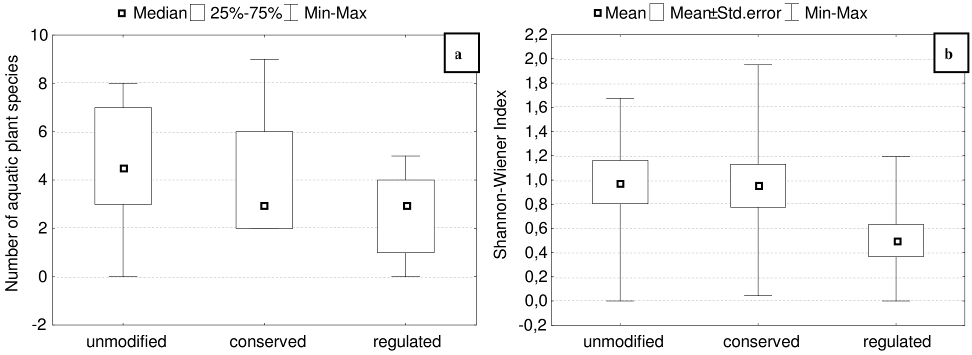


Fig. 1. Diversification of the number of species (a) and species variety Index Shannon-Wiener (b) in the examined sections

The highest mean number of species was observed in natural sections while in modified sections especially those which were regulated a lot less. Values of the diversity Index by Shannon-Wiener observed in compared sections were slightly different. In unmodified and conserved examined sections they were similar while in regulated watercourses they were considerably lower. The mean index value in unmodified, conserved and regulated river beds was calculated at 0.98; 0.95 and 0.5 respectively. Using results of the following research ecological risk factors - *P* and *S* - were defined and classified (Tables 1 and 2).

Table 1

Scale of the changes occurrence probability in the aquatic plant communities in the river beds as a result of the watercourses regulation and maintenance works - *P*

Probability of changes occurrence	
Point scale	**Description scale**
1 Very low	Slopes mowing, river bed elutriation with the removal of the aquatic plants.
2 Low	Slopes mowing, river bed elutriation with the removal of the aquatic plants, reparation and completing fascine strengthening.
3 Medium	Changes in cross-section parameters, modification of scarps incline to 1:1.5 and more, strengthening the foundation of riverbank with fascine.
4 High	Changes in cross-section parameters, strengthening scarps with stone or net stone mattresses coatings.
5 Very high	Changes in cross-section parameters, modification of vertical section with horizontal scarps, strengthening slopes with net stone baskets or retaining walls.

Table 2

The scale of the consequences of the watercourses regulation and maintenance works in the river bed for the aquatic plant communities - *S*

Susceptibility to changes in aquatic plant species composition	
Point scale	**Description scale**
1 Lack	There are no hydromacrophytes in the watercourse.
2 Mild	There are 1-3 species of hydromacrophytes with low and medium index values $W = 1$ or 2 in the watercourse.
3 Moderate	There are above 4 species of hydromacrophytes with dominating taxons of a low index value $W = 1$ in the watercourse.
4 Severe	There are above 4 species of hydromacrophytes with dominating taxons of a medium index value $W = 2$ in the watercourse.
5 Very severe	There are taksons with high index value $W = 3$ in the watercourse.

Classifications of considered risk factors showed in Tables 1 and 2 formed a basis to compile ecological risk matrix in both maintained and conserved watercourses (Fig. 2).

The following matrix shows the level of risk may be placed between 1 and 25 points. Information obtained during the field work was used for determination of point range for small risk - usually accepted, medium and high - unaccepted. Each section located in modified watercourses was defined with the area of matrix where observed changes in plants communities took place (Fig. 3). The matrix was also marked with the direction of the observed changes referring to the number of species and Shannon-Wiener index. In case of conservatory works the most common situations were those with a growth in both values

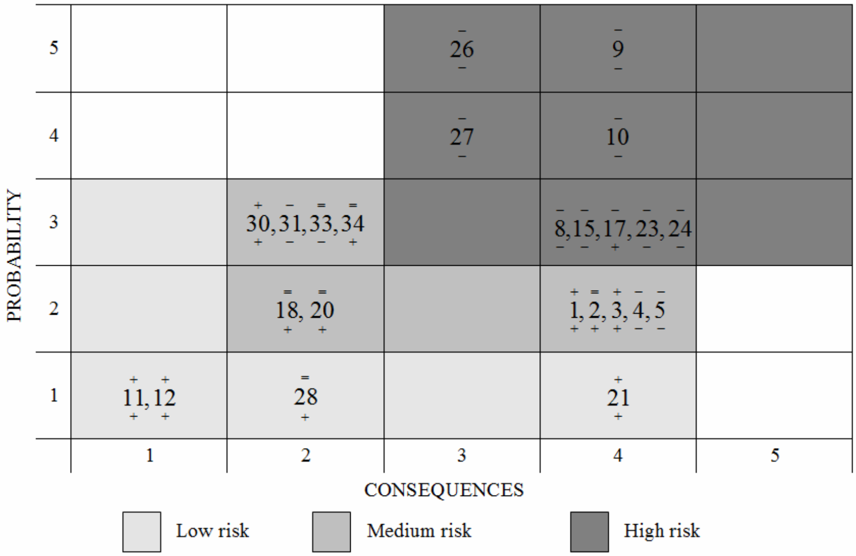
Regulated sections in most cases show that the result of river beds regulation is lowering the number of species of aquatic plants and the values of Shannon-Wiener index. This served as a basis for ecological risk classification taking into account its 3 levels - low, medium and high risk.

PROBABILITY

5	5	10	15	20	25
4	4	8	12	16	20
3	3	6	9	12	15
2	2	4	6	8	10
1	1	2	3	4	5
	1	**2**	**3**	**4**	**5**

CONSEQUENCES

Fig. 2. Matrix of ecological risk in maintained and regulated watercourses



PROBABILITY

5			$\overset{-}{\underset{-}{26}}$	$\overset{-}{\underset{-}{9}}$	
4			$\overset{-}{\underset{-}{27}}$	$\overset{-}{\underset{-}{10}}$	
3		$\overset{+}{\underset{+}{30}}, \overset{-}{\underset{-}{31}}, \overset{=}{\underset{-}{33}}, \overset{=}{\underset{+}{34}}$		$\overset{-}{\underset{-}{8}}, \overset{-}{\underset{-}{15}}, \overset{-}{\underset{+}{17}}, \overset{-}{\underset{-}{23}}, \overset{-}{\underset{-}{24}}$	
2		$\overset{=}{\underset{+}{18}}, \overset{=}{\underset{+}{20}}$		$\overset{+}{\underset{+}{1}}, \overset{=}{\underset{+}{2}}, \overset{+}{\underset{+}{3}}, \overset{-}{\underset{-}{4}}, \overset{-}{\underset{-}{5}}$	
1	$\overset{+}{\underset{+}{11}}, \overset{+}{\underset{+}{12}}$	$\overset{=}{\underset{+}{28}}$		$\overset{+}{\underset{+}{21}}$	
	1	2	3	4	5

CONSEQUENCES

[ ] - shows a trend of changes in the number of species: „+" - increase, „–" - decrease, „=" - no changes
28 - the number of the examined section
[ ] - shows a trend of changes in the Shannona-Wienera index: „+" - increase, „–" - decrease

Fig. 3. Ecological risk classification on the basis of alternations in aquatic plants communities in maintained and regulated watercourses

Conclusions

1. The range of performed works and ecological tolerance of the plants occurrence in watercourses had a big influence on the size of alternations in the aquatic plants communities.
2. Basing on the risk matrix ecological risk was classified in three different levels. Low risk was determined ranging from 1 to 4, medium risk was found between 4 and 8 while high risk was determined at the level of 9 points or more.
3. Performed analysis showed that maintenance works are connected with low or moderate risk. Regulatory works comprise moderate or high risk area.
4. In order to limit adverse alternations in aquatic plants community risk assessment should be performed when planning works. It requires detailed environmental valorization in the river bed and detailed analysis of the range of planned works.

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KLASYFIKACJA RYZYKA EKOLOGICZNEGO W REGULOWANYCH I KONSERWOWANYCH CIEKACH

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Abstrakt: Przedmiotem pracy jest ryzyko ekologiczne w robotach regulacyjnych i konserwacyjnych wykonywanych na małych i średnich ciekach nizinnych. Ryzyko to nie jest jeszcze rozpoznane w stopniu pozwalającym projektantom oraz wykonawcom robót na podjęcie działań mających na celu jego ograniczanie. W pracy przedstawiono propozycję rozwiązania tego problemu na przykładzie zmian w zbiorowiskach naczyniowych roślin wodnych. Podstawę analizy stanowią wyniki badań terenowych prowadzonych w latach

2007-2008 na 10 uregulowanych, konserwowanych oraz nieprzekształconych nizinnych ciekach Dolnego Śląska. Badania obejmowały identyfikację występujących w korycie gatunków naczyniowych roślin wodnych oraz określenie stopnia pokrycia przez nie dna. Wykazały one, że w następstwie prac regulacyjnych i konserwacyjnych zachodzą zmiany jakościowe i ilościowe w zbiorowiskach naczyniowych roślin wodnych. Analiza tych zmian, z uwzględnieniem zakresu oraz warunków wykonania robót, pozwoliła na przypisanie miar czynnikom rozpatrywanego ryzyka. Stanowiło to podstawę opracowania macierzy klasyfikacji ryzyka. Przyjęto w niej 3 poziomy ryzyka - niskie, umiarkowane oraz wysokie.

Słowa kluczowe: ryzyko ekologiczne, naczyniowe rośliny wodne, roboty konserwacyjne, regulacja cieków

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CHEMISTRY OF TAP WATER IN SELECTED LOCALITIES ON SOUTH PODLASIE LOWLAND

CHEMIZM WODY WODOCIĄGOWEJ W WYBRANYCH MIEJSCOWOŚCIACH NIZINY POŁUDNIOWOPODLASKIEJ

Abstract: The aim of this paper is presentation of results of chemical composition of tap water in selected localities on South Podlasie Lowland. Samples of water were taken from water treatment station and taps situated in various parts of Lukow, Sokolow Podlaski and selected localities in Lochow, Wierzbno and Mokobody commune. Quarterly investigations covered analysis of water reaction (pH) by potentiometric method, electrical conductivity (EC) by electrochemical method and total concentration of 26 elements by inductively coupled plasma atomic emission spectrometry (ICP-AES). It was found that untreated waters being the source of tap water in selected localities on South Podlasie Lowland contained excessive iron and manganese amounts, that were efficiently removed during the treatment. Concentration of analyzed elements in treated water did not exceed the permissible limits and quality of analyzed tap water changed a little during its transport due to the secondary contamination.

Keywords: tap water chemistry, ICP-AES, quality indicators of tap water

„There is no life without water. It is a treasure indispensable to all human activity. Fresh water resources are not inexhaustible. It is essential to conserve, control, and wherever possible, to increase them. The quality of water must be maintained at levels suitable for the use to be made of it and, in particular, must meet appropriate public health standards. Conservation of water calls for intensified scientific research, training of specialists and public information services". European Water Charter proclaimed in Strasbourg, May 6, 1968 considers that collective action on a European scale on water problems is necessary. On a local scale, underground water resources and quality are of great importance to public health and local economy. These waters are main reservoir of drinking water for people, water for industry, agriculture, food production and food processing. Water intended for these purposes must comply with the requirements presented in appropriates legal acts [1, 2]. Among these requirements important role play physicochemical indexes of water quality. Physical, chemical, and biochemical processes affecting the quality of water supplied to the receivers occur in tap water distribution systems. The water quality often gets worse during its flow from the intake and treatment point to the receiving point (tap). Chemically and biologically instable waters are mostly exposed to the secondary contamination, because they make a corrosion of metal elements of the water distribution system and internal installations. The aim of this paper is presentation of results of chemical composition of tap water in selected localities on South Podlasie Lowland.

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Material and methods

Samples of water were taken from water treatment stations (untreated and treated water) and taps situated in various parts of Lukow (15 samples), Sokolow Podlaski (8 samples), selected localities in Lochow commune (7 samples), Wierzbno commune (9 samples) and Mokobody commune (15 samples). Quarterly investigations covered analysis of water reaction (pH) by potentiometric method, electrical conductivity (EC) by electrochemical method and total concentration of 26 elements by inductively coupled plasma atomic emission spectrometry (ICP-AES) [3]. The study was carried out with the Optima 3200RL by Perkin Elmer. The optics of the instrument consists of a high resolution, Echelle-based polychromator, a segmented-array charge-coupled device (SCD) detects the light. A cross-flow nebuliser with GemTips was used throughout the study. The working parameters of the apparatus were: RF power - 1300 W, plasma argon flow rate - 15 dm^3/min, auxiliary argon flow rate - 0.5 dm^3/min, nebuliser argon flow rate - 0.8 dm^3/min, sample flow rate - 1.5 cm^3/min, integration time - 30 s. The element detection limits at the analytical wavelengths are presented in Table 1. For the calibration of the elements, multielement standards were mixed from single element stock solutions (Fluka). All samples as well as standards and the blank were acidified to contain 2% nitric acid in the final solution. Acid used was Riedel-de Haën. 18 MΩ water was used for dilution and calibration blank.

Table 1

Analytical wavelengths of analyzed elements and method detection limits

Element	Wavelength [nm]	Detection limit [$mg \cdot dm^{-3}$]
P	213.617	0.05
K	766.490	0.005
Ca	317.933	0.006
Mg	285.213	0.002
Na	330.237	0.8
S	181.975	0.06
Fe	238.204	0.002
Al	394.401	0.02
Mn	257.610	0.0004
Co	228.616	0.001
Mo	202.031	0.001
B	249.677	0.0004
Li	670.784	0.001
Ti	334.940	0.001
Ba	233.527	0.006
Sr	421.552	0.0001
V	290.880	0.001
Se	196.026	0.05
Sn	189.927	0.08
As	188.979	0.02
Pb	220.353	0.008
Cd	228.802	0.0009
Cr	267.716	0.001
Cu	327.393	0.005
Zn	206.200	0.008
Ni	231.604	0.002

Results and discussion

Performed studies revealed that water samples from analyzed water supply systems were characterized by stable acidity and specific conductivity, and values of these parameters met the requirements of legal acts and WHO recommendations [1, 2, 4]. Concentrations of 13 analyzed elements (P, Pb, Cd, Ni, As, Cr, Sn, Al, Co, Mo, Ti, V, Se) were below detectable limits for methods presented in Table 1, while concentrations of other analyzed elements are presented in Tables 2 and 3.

Table 2

Physicochemical parameters of untreated, treated and mean, minimal, maximal values in tap water supply systems in Lukow, Sokolow Podlaski, Lochow, Wierzbno and Mokobody commune

		pH	**EC**	**Ca**	**Mg**	**K**	**Na**	**S**
		-	**[$\mu S\cdot cm^{-1}$]**	**[$mg\cdot dm^{-3}$]**				
Lukow	untreated	7.4	329	68.3	6.19	1.97	3.63	0.42
	treated	7.3	312	64.6	5.95	1.85	3.37	0.31
	mean	7.4	338	66.0	6.02	1.89	3.56	0.34
	min	7.3	311	65.0	5.93	1.85	3.37	0.28
	max	7.6	345	67.4	6.11	2.33	3.73	0.48
	SD*	0.1	8	0.8	0.05	0.12	0.12	0.05
	RSD*	0.9	2.4	1.2	0.9	6.3	3.2	13.8
Sokolow Podlaski	untreated	7.3	535	97.6	15.5	2.05	8.82	0.97
	treated	7.3	510	95.6	15.1	1.92	8.25	1.17
	mean	7.3	522	95.0	15.1	1.90	8.11	1.31
	min	7.2	508	92.5	14.9	1.86	7.96	1.01
	max	7.6	544	98.4	15.9	1.97	8.27	1.46
	SD	0.1	12	1.7	0.3	0.04	0.11	0.14
	RSD	1.8	2.2	1.7	2.1	2.2	1.4	11.0
Lochow	untreated	7.0	407	69.1	8.84	1.71	6.53	3.41
	treated	7.1	402	69.1	8.88	1.60	6.48	3.39
	mean	7.0	399	69.4	8.94	1.59	6.58	3.27
	min	7.0	397	69.0	8.85	1.56	6.45	2.73
	max	7.1	403	70.1	9.08	1.64	6.83	3.55
	SD	0.1	2	0.4	0.09	0.03	0.13	0.33
	RSD	0.8	0.5	0.6	1.0	1.9	2.0	10.1
Wierzbno	untreated	7.3	536	92.0	15.4	1.58	4.83	2.92
	treated	7.6	482	90.5	15.6	1.67	4.59	2.79
	mean	7.5	491	88.6	15.3	1.72	5.06	2.89
	min	7.4	472	82.8	13.9	1.66	4.66	2.65
	max	7.6	500	93.9	16.4	1.82	5.45	4.02
	SD	0.1	8	3.0	0.7	0.06	0.23	0.43
	RSD	0.9	1.6	3.4	4.4	3.4	4.6	14.8
Mokobody	untreated	7.9	571	-**	-	-	-	-
	treated	8.0	563	-	-	-	-	-
	mean	7.4	595	111	16.8	2.22	6.85	14.3
	min	6.5	560	99.5	14.8	1.38	4.88	8.53
	max	7.8	839	145	17.6	2.57	18.4	18.5
	SD	0.3	45	6.64	0.54	0.20	2.57	1.99
	RSD	3.8	7.5	6.0	3.2	9.2	37.5	14.0

* SD - standard deviation, RSD - relative standard deviation

** not analyzed

Table 3

Chemical parameters of untreated, treated and mean, minimal, maximal values in tap water supply systems in Lukow, Sokolow Podlaski, Lochow, Wierzbno and Mokobody commune

		Fe	**Mn**	**B**	**Li**	**Ba**	**Sr**	**Cu**	**Zn**
		[mg·dm^{-3}]							
Lukow	untreated	1.108	0.170	0.032	0.007	0.033	0.392	0.003	0.009
	treated	0.123	0.050	0.031	0.006	0.026	0.379	0.001	0.008
	mean	0.109	0.012	0.029	0.005	0.025	0.389	0.009	0.399
	min	0.099	0.006	0.028	0.004	0.022	0.382	0.003	0.100
	max	0.136	0.027	0.031	0.007	0.026	0.396	0.029	1.269
	SD*	0.011	0.007	0.001	0.001	0.001	0.004	0.008	0.307
	RSD*	9.7	52.2	2.3	16.1	3.4	1.1	90.9	76.8
Sokolow Podlaski	untreated	0.513	0.143	0.045	0.011	0.042	0.250	0.001	0.006
	treated	0.009	0.004	0.045	0.010	0.038	0.233	0.001	0.061
	mean	0.011	0.003	0.038	0.010	0.039	0.233	0.044	0.896
	min	0.005	0.002	0.035	0.009	0.037	0.223	0.003	0.353
	max	0.025	0.008	0.045	0.011	0.043	0.263	0.096	2.470
	SD	0.007	0.002	0.004	0.001	0.002	0.013	0.032	0.696
	RSD	66.0	61.4	9.8	7.3	5.2	5.4	73.6	77.7
Lochow	untreated	1.489	0.563	0.032	0.004	0.045	0.196	0.009	0.019
	treated	0.061	0.047	0.032	0.004	0.035	0.197	0.027	0.049
	mean	0.030	0.008	0.031	0.004	0.034	0.198	0.008	0.236
	min	0.017	0.002	0.031	0.004	0.032	0.195	0.005	0.105
	max	0.058	0.022	0.033	0.004	0.035	0.201	0.012	0.528
	SD	0.013	0.007	0.001	0.000	0.001	0.003	0.002	0.170
	RSD	44.3	86.1	2.7	2.9	3.2	1.3	26.6	72.2
Wierzbno	untreated	0.744	0.333	0.016	0.008	0.156	0.264	0.001	0.023
	treated	0.047	0.003	0.017	0.008	0.133	0.261	0.001	0.027
	mean	0.055	0.005	0.018	0.008	0.128	0.260	0.172	1.040
	min	0.047	0.002	0.017	0.007	0.100	0.240	0.004	0.202
	max	0.076	0.012	0.020	0.010	0.137	0.286	0.935	2.277
	SD	0.010	0.004	0.001	0.001	0.011	0.014	0.299	0.767
	RSD	18.1	78.2	4.6	9.1	8.8	5.2	173.3	73.7
Mokobody	untreated	1.85	0.153	-**	-	-	-	-	-
	treated	0.06	0.008	-	-	-	-	-	-
	mean	0.008	0.004	0.025	0.008	0.066	0.250	0.018	1.51
	min	0.003	0.001	0.017	0.002	0.028	0.173	0.002	0.123
	max	0.043	0.037	0.056	0.013	0.082	0.332	0.093	9.47
	SD	0.007	0.006	0.007	0.002	0.011	0.038	0.018	1.89
	RSD	79.7	130.3	28.0	29.1	16.3	15.3	102.1	125.2

* SD - standard deviation, RSD - relative standard deviation

** not analyzed

Concentrations of K, Ca, Mg, Na, S, B, Li, Ba, and Sr in water samples from intake points slightly varied and differed a little from those in untreated and treated water samples at the inlet to the water supply system. The greatest changes during the water transport along with quite large concentration differences were recorded for Fe, Mn, Cu, and Zn. It was found that mean iron concentration in untreated water samples from Lukow, Sokolow Podlaski, Lochow, Wierzbno and Mokobody exceeded permissible values amounting to 1.11, 0.513, 1.49, 0.744, 1.85 mg · dm^{-3}, respectively. The excessive quantities of the metal were removed during the treatment processes, when its concentration reductions were by

89, 98, 96, 94 and 97%. Treated water supplied to the system met requirements for that parameter. Water taken from the taps did not contain the excessive iron contents in any water supply system studied (Table 3). Also manganese concentration in water taken from underground layers excessive permissible norms amounting 0.170 mg $\cdot$ dm^{-3} in Lukow, 0.143 mg $\cdot$ dm^{-3} in Sokolow Podlaski, 0.563 mg $\cdot$ dm^{-3} in Lochow, 0.333 mg $\cdot$ dm^{-3} in Wierzbno and 0.153 mg $\cdot$ dm^{-3} in Mokobody. The demanganation process resulted in the decrease of manganese concentrations by 71, 97, 92, 99, 95%, respectively for the communes, which allowed for reaching lower value than permissible one. Water supplied to the distribution systems in Sokolow Podlaski, Wierzbno and Mokobody contained traces of manganese and its quality did not change during the transport. The element concentration was higher in water from treatment plant in Lukow and Lochow, but its decrease occurred due to the manganese compounds precipitation within water supply system. Waters from Lukow, Sokolow Podlaski, Lochow and Wierzbno contained traces of zinc (0.009, 0.006, 0.019, 0.023 mg $\cdot$ dm^{-3}, respectively). Mean zinc concentrations in water samples from the taps were higher (0.399, 0.896, 0.236, 1.04 mg $\cdot$ dm^{-3}); however they did not exceed values recommended by WHO. Quite broad range of these element concentrations in water samples from particular intake points was recorded, which was probably associated with the contamination due to materials, the terminal connections are made of. Mean copper concentrations in untreated water samples were from 0.002 to 0.009 mg $\cdot$ dm^{-3}. Water taken at intake points (taps) contained slightly more metal, namely in systems in Wierzbno and Sokolow Podlaski communes, but maximum values were much lower than permissible level. The differences of copper concentrations in samples resulted from copper installations in some intake points.

Conclusions

1. The underground waters being the source of tap water in selected localities on South Podlasie Lowland were characterized by good quality. They contained excessive iron and manganese amounts, that were efficiently removed during the treatment.
2. Quality of treated water supplied to the distribution systems in Lukow, Sokolow Podlaski, Lochow, Wierzbno and Mokobody met all norms for the quality indicators studied.
3. Quality of analyzed tap water changed a little during its transport due to the secondary contamination. No excessive concentrations of studied elements were recorded. The water quality slightly worsened in reference to zinc and copper contents, namely at intake points, where galvanized steel or copper pipes were the part of installations.

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CHEMIZM WODY WODOCIĄGOWEJ W WYBRANYCH MIEJSCOWOŚCIACH NIZINY POŁUDNIOWOPODLASKIEJ

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Abstrakt: Celem niniejszej pracy jest przedstawienie wyników analizy składu chemicznego wody wodociągowej dostarczanej mieszkańcom wybranych miejscowości Niziny Południowopodlaskiej. Punkty pobrania próbek do badań wyznaczono na wyjściu ze stacji uzdatniania oraz w kurkach czerpalnych, położonych w różnych dzielnicach Łukowa i Sokołowa Podlaskiego, a także w różnych miejscowościach gmin Łochów, Wierzbno i Mokobody. Próbki wody pobierano w odstępach kwartalnych. W pobranych próbkach oznaczono odczyn (pH) wody metodą potencjometryczną, przewodnictwo właściwe metodą elektrochemiczną oraz stężenie K, Ca, Mg, Na, S, Fe, Mn, B, Li, Ba, Sr, Cu, Zn, Ni metodą optycznej spektrometrii emisyjnej ze wzbudzeniem w plazmie sprzężonej indukcyjnie (ICP-AES). Stężenie pierwiastków objętych badaniami na ogół nie przekraczało obowiązujących wartości dopuszczalnych. Sporadycznie odnotowano podwyższone wartości analizowanych parametrów w próbkach wody pobieranych w kurkach czerpalnych, wskazujące na zanieczyszczenie wody w systemie dystrybucji. W wodzie surowej stwierdzono ponadnormatywne stężenia żelaza i manganu, ale pierwiastki te były skutecznie usuwane w procesie uzdatniania.

Słowa kluczowe: chemizm wody wodociągowej, ICP-AES, wskaźniki jakości wody wodociągowej

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MODELING OF CHROMIUM(III) AND CHROMIUM(VI) RETENTION COEFFICIENT IN POLYELECTROLYTE ENHANCED ULTRAFILTRATION

MODELOWANIE WSPÓŁCZYNNIKA RETENCJI CHROMU(III) I CHROMU(VI) W ULTRAFILTRACJI WSPOMAGANEJ POLIELEKTROLITEM

Abstract: Effectiveness of polyelectrolyte-enhanced ultrafiltration in chromium recovery from its aqueous solutions was tested experimentally. Two chromium species, Cr(III) and Cr(VI) ions, were the subject of ultrafiltration processes enhanced with two water-soluble, ion-exchanging polyelectrolytes. These were: poly(sodium 4-styrenesulfonate) - PSSS (for Cr(III) ions recovery) and poly(diallyldimethylammonium chloride) - PDDAC (for Cr(VI) ions recovery). Experimental ultrafiltration tests with the model analytical solutions of appropriate chromium ions (5 and 50 mg dm^{-3}), at different pH and with various polyelectrolyte doses, provided numerical data for the artificial neural networks training procedure. Numerical neural network models made prediction of chromium retention coefficient (*R*) under different process conditions (pH, polymer dose, concentration of selected Cr form) possible. Strongly non-linear dependencies of retention coefficient (*R*) on pH and polymer : metal concentration ratio for both chromium species, represented by experimental data, were identified and modeled by neural networks correctly. Good compatibility between experimental data and neural network predictions was observed.

Keywords: polyelectrolyte enhanced ultrafiltration (PEUF), Cr(III), Cr(VI), poly(sodium 4-styrenesulfonate), poly(diallyldimethylammonium chloride)

Over the last years, the *polymer enhanced ultrafiltration* (PEUF), used to separate heavy metal ions from their water solutions, has been gaining in popularity. The process is based on binding the metal ions by water-soluble chelating polymers or polyelectrolytes containing ion-exchange groups, followed by their retention on ultrafiltration membrane. Normally, the ultrafiltration separation of metals is enhanced by macromolecules containing amino (chitosan, polyethyleneimine), carboxyl (poly(acrylic acid), its salts and copolymers) or hydroxyl (poly(vinyl alcohol)) groups [1-3]. Polymer enhanced ultrafiltration has been successfully applied to the separation of chromium from aqueous solutions, both Cr(III) and Cr(VI) [4-9]. Promising effects corresponded to binding Cr(III) with poly(acrylic acid) or its copolymer with maleic acid [5, 6], chitosan, pectin, polyethyleneimine and ethoxylated polyethyleneimine [4, 6, 7]. Polyethyleneimine appeared also to be an effective agent in enhancing the ultrafiltration separation of Cr(VI), due to the anion-exchange nature of the primary, secondary and tertiary amino groups present in its structure [5, 6]. Similar effect was achieved in ultrafiltration of Cr(VI) with addition of modified starch having cationic functional groups, capable of reacting with contaminants of anionic nature [8]. Relying on literature reports and own research [5], the authors suggested ultrafiltration removal of Cr(III) and Cr(VI) ions enhanced with polyelectrolytes which contain functional groups of strong ion-exchange properties.

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Poly(*sodium 4-styrenesulfonate*) - PSSS, ~~a~~ water-soluble polymer which contains sulfonic groups capable of binding metal cations (Cr(III)) and *poly*(*diallyldimethylammonium chloride*) - PDDAC, whose quaternary ammonium groups exhibit anion-exchange properties (Cr(VI)) were selected for the process [9].

The work demonstrates possibility of application of artificial neural networks trained on experimental data sets for accurate prediction of the effectiveness of Cr(III) and Cr(VI) separation (expressed by chromium retention coefficient, *R*) in diverse process conditions (environment's pH, polymer : metal concentration ratio, initial Cr concentration and its chemical form).

Materials and methods

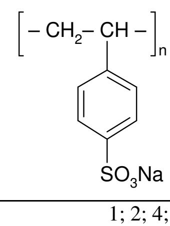
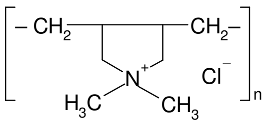
Model solutions of Cr(III) and Cr(VI) ions, of concentrations 5 and 50 mg dm^{-3}, were prepared using analytical grade chromium(III) nitrate $Cr(NO_3)_3 \cdot 9H_2O$ and potassium dichromate $K_2Cr_2O_7$ (POCh S.A., Gliwice, Poland).

Water soluble polyelectrolytes: poly(sodium 4-styrenesulfonate) - PSSS (M_w = 70 kDa, 30% solution) and poly(diallyldimethylammonium chloride) - PDDAC (M_w = 100÷200 kDa, 20% solution), Sigma-Aldrich, were used as Cr(III) and Cr(VI) binding agents. In order to remove small molecules, polyelectrolytes were preliminarily diafiltrated using UF membrane.

The set of polymer-chromium solutions of different molar concentration ratios (mol of mer unit per mol of metal) were prepared by mixing the appropriate doses of suitable polyelectrolytes with the proper chromium species. Process environment's pH adjustment to the required level, within the 1-10 range, was done with the use of 1 mol dm^{-3} NaOH and HNO_3 solutions (POCh S.A.). More detailed characteristic of the solutions is presented in Table 1.

Table 1

Characteristic of the solutions used in ultrafiltration tests

Chromium ion	Cr(III)		Cr(VI)	
Polyelectrolyte		PSSS poly(sodium 4-styrene-sulfonate)	 PDDAC poly(diallyldimethylammonium chloride)	
pH	1; 2; 4; 6; 8; 10		1; 2; 4; 6; 8; 10	
Chromium concentration	5 mg dm^{-3}	50 mg dm^{-3}	5 mg dm^{-3}	50 mg dm^{-3}
Polymer : metal molar concentration ratio, *Pol.:Met.*	2.5; 5; 7.5; 10	5; 7,5; 10; 12.5	0.5; 1; 2.5; 5; 7.5; 10	1; 2.5; 5; 7.5; 10; 12.5

Prepared solutions were a subject of ultrafiltration tests in AMICON 8400 membrane cell, equipped with magnetic stirrer. Ultrafiltration membrane HZ20 (GE Osmonics), made of polysulfone, was used in the separation processes. Water permeability coefficient of the membrane, determined experimentally, was $2.1 \cdot 10^{-10}$ m^{3}m^{-2}s^{-1}Pa^{-1}. Transmembrane pressure of 1 bar was applied in the ultrafiltration tests. The effectiveness of polymer enhanced ultrafiltration was evaluated by measurement of chromium concentrations in the permeate and in the feed (*Atomic Absorption Spectrometer* SpectrAA 880, Varian) followed by calculation of chromium retention coefficient (R) according to the formula: $R = 1 – C_P/C_F$, where: C_P, C_F - chromium concentrations in the permeate and in the feed, respectively. Detection limit for chromium ions analysis was 0.005 mg dm^{-3}.

Calculations

Raw experimental data matrixes collected, matching chromium separation efficiencies (R) with various combinations of Cr initial concentrations, *Pol.:Met.* molar ratios and ultrafiltration process environment's pH provided basis for the artificial neural networks creation, followed by their training, validating and testing procedures. Computations were done with the use of *STATISTICA Neural Networks* software. Various network types were preliminary tested, including: *radial basis function* (RBF) networks, *general regression neural networks* (GRNN), *multilayer perceptrons* (MLP) and *linear* ones. Each net structure was trained with appropriate algorithms (pseudoinversion, sub-sample, conjugate gradient and backpropagation error), both independently and/or in various sequences. Two optimal net structures were identified using statistical indicators. For the network modeling ultrafiltration process on HZ20 membrane with PSSS polymer in a form of $R = f(C_{met}, Pol.:Met., pH)$ it was MLP type network of 3-9-8-1 structure (three inputs representing: C_{met}, $Pol.:Met., pH$, one output neuron (R), with two hidden neuron layers with 9 neurons in the first and 8 in the second one), trained by 100 iterations with *backpropagation error* algorithm (BP) followed by additional training covering 59 cycles with the *conjugate gradient* (CG) algorithm (resulting *mean deviation* MD = –0.0085, *root mean square deviation* RMSD = 0.0552). In case of artificial neural network modeling ultrafiltration behavior of HZ20 - PDDAC - Cr(VI) system, the best model structure proved to be multilayer perceptron of 3-3-1 structure (3 inputs, one hidden layer with 3 neurons and one output neuron), trained with 100 backpropagation error iterations followed by 61 conjugate gradient cycles (resulting MD = 0.0074, RMSD = 0.0654). These two optimal neural network configurations were then used for numerical simulation of the polyelectrolyte enhanced ultrafiltration process, especially for the identification of complex influence of various combinations of process parameters on chromium forms retention effectiveness.

Results and discussion

Figures 1 and 2 present the neural network simulation results with respect to both chromium species, their initial concentrations and the appropriate polymers used.

The $R = f(Pol.:Met., pH)_{Cmet.}$ response surfaces, based on neural network predictions for selected data matrixes representing the assumed process conditions, demonstrate essential, strongly nonlinear influence of both parameters under study (pH, polymer dose), as well as concentration, chemical form of chromium in its initial solution and the added polyelectrolyte type on the ultrafiltration process effectiveness. The steep increase in $R = f(pH)_{Pol:Met,Cmet}$ function values with the increase in alkalinity of solution, compatible with the experimental data results, is demonstrated clearly, especially within the pH 1÷4 (Cr(III)) and 1÷6 (Cr(VI)) ranges at small polyelectrolyte doses.

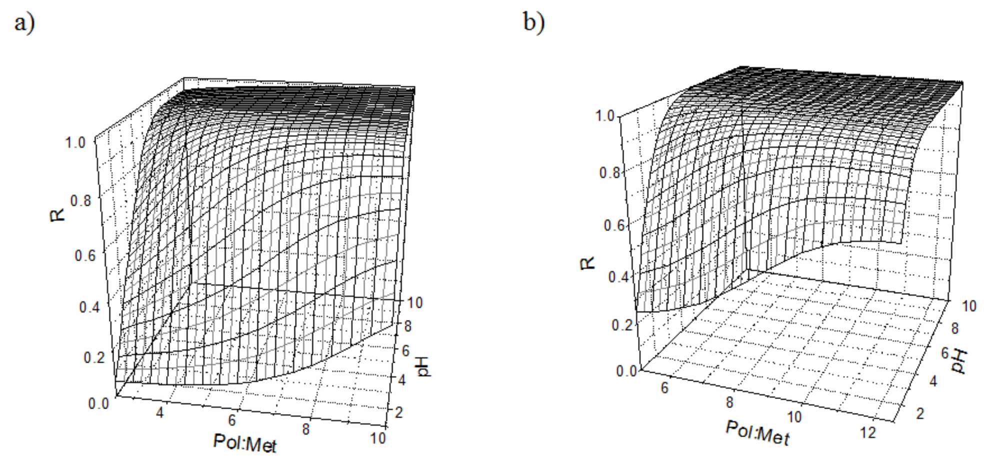


Fig. 1. Neural network model predictions - dependence of Cr(III) retention coefficient (*R*) on polymer: metal concentration ratio (*Pol.:Met.*) and process environment's pH. Initial Cr(III) concentrations: 5 mg dm^{-3} (a) and 50 mg dm^{-3} (b), polyelectrolyte - PSSS

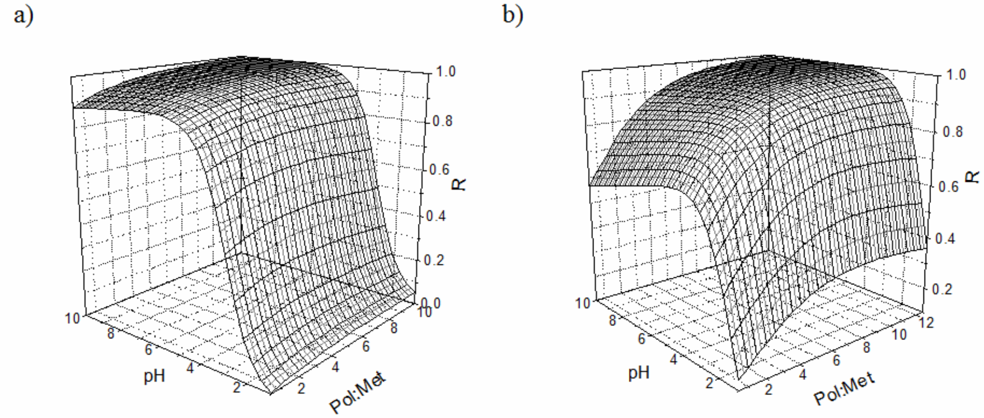


Fig. 2. Neural network model predictions - dependence of Cr(VI) retention coefficient (*R*) on polymer : metal concentration ratio (*Pol.:Met.*) and the process environment's pH. Initial Cr(VI) concentrations: 5 mg dm^{-3} (a) and 50 mg dm^{-3} (b), polyelectrolyte - PDDAC

Similar $R = f(Pol.:Met.)_{pH, C_{met}}$ function dependency can be observed, especially for all Cr(III) solutions and for higher Cr(VI) concentrations. As a result, systematic increase in *R* is observed, corresponding to the increase in polyelectrolyte dose, up till attaining the maximal, stable metal retention effect, which for Cr(VI) solutions of concentration 50 mg dm^{-3} corresponds to *Pol.:Met.* > 5, whereas in case of Cr(III) solutions it is attained at various *Pol.:Met.* values, depending in a complex way also on pH value and concentration of metal in initial solution. In case of Cr(VI) solution of concentration 50 mg dm^{-3}, the $R = f(pH)_{Pol.:Met.,Cmet}$ function for *Pol.:Met.* < 5 reaches clear maximum, corresponding to pH approx. 5-6. In a more alkaline environment visible decrease of *R* value is observed. For *Pol.:Met.* > 6 this extreme becomes more and more diffuse and after reaching the maximum small decline in *R* is only reported. Comparing both neural network response surfaces, attributed to two concentrations (5 and 50 mg dm^{-3}) and corresponding to some selected chromium form, in solutions of higher Cr concentrations within the low pH values (ca 1-2) - for a constant *Pol.:Met.* ratio - one can notice also higher values of metal retention coefficient, *R*. On the other hand it should be noted, that Cr(III) solutions of concentration 50 mg dm^{-3} required application of larger polyelectrolyte doses than Cr(III) solutions of concentration 5 mg dm^{-3}, resulting from formation of precipitates, observed within the range of *Pol.:Met.* < 2.5 and < 5, for 5 and 50 mg Cr(III) dm^{-3}, respectively.

Conclusions

Essential influence of polymer dose and environment's pH on Cr(III) and Cr(VI) separation efficiency in the ultrafiltration process enhanced by polyelectrolytes of strong ion-exchange properties was demonstrated.

The numerical $R = f(Pol.:Met., pH)_{Cmet}$ function response surfaces, elaborated on the basis of neural network models simulation results, identified clearly (for both chromium forms and their concentrations used) the existence of some pH - *Pol.:Met.* regions, within which metal retention processes can run with very high efficiency, $R \approx 1$ (corresponding to plateau ranges noticeable in Figs. 1 and 2).

Numerical artificial neural network models presented can be regarded as a helpful tool in design works, especially concerning optimization of metals removal in polyelectrolyte enhanced ultrafiltration processes in various environment protection applications.

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MODELOWANIE WSPÓŁCZYNNIKA RETENCJI Cr(III) I Cr(VI) W ULTRAFILTRACJI WSPOMAGANEJ POLIELEKTROLITEM

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Abstrakt: Przedstawiono możliwości prognozowania efektywności separacji chromu z roztworów wodnych w procesie ultrafiltracji wspomaganej działaniem polielektrolitu, korzystając ze sztucznej sieci neuronowej. Badaniom poddano układy zawierające dwie różne formy chromu - Cr(III) i Cr(VI). Do wspomagania ultrafiltracyjnej separacji metalu wykorzystano dwa rozpuszczalne w wodzie polimery o właściwościach jonowymiennych - poli(4-styrenosulfonian sodu), PSSS (separacja Cr(III)) oraz poli(chlorek diallilodimetyloamoniowy), PDDAC (separacja Cr(VI)). Wyniki testów ultrafiltracji przeprowadzonej dla wodnych roztworów modelowych obu form chromu o stężeniach 5 i 50 mg dm^{-3}, przy różnych wartościach pH środowiska oraz zróżnicowanych dawkach właściwych polielektrolitów, stanowiły podstawę uczenia i testowania struktur obliczeniowych sztucznych sieci neuronowych, umożliwiających predykcję współczynnika retencji (*R*) danej formy chromu dla różnych warunków procesowych (pH, dawka wybranego polimeru, stężenie wybranego jonu Cr). Na podstawie wyników doświadczalnych oraz opracowanych sieciowych modeli numerycznych zidentyfikowano istotny, mocno nieliniowy wpływ pH oraz stosunku stężeń polimer : metal na wartości współczynników retencji (*R*) obu form chromu. Uzyskano dobrą zgodność danych eksperymentalnych z wartościami wyznaczonymi za pomocą sztucznej sieci neuronowej.

Słowa kluczowe: ultrafiltracja wspomagana polielektrolitem (PEUF), Cr(III), Cr(VI), poli(4-styrenosulfonian sodu), poli(chlorek diallilodimetyloamoniowy)

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INFLUENCE OF CHOSEN INSECTICIDES ON THE CHARACTERISTICS OF VERMICOMPOST PRODUCED FROM KITCHEN WASTE

WPŁYW WYBRANYCH INSEKTYCYDÓW NA CECHY WERMIKOMPOSTÓW WYPRODUKOWANYCH Z ODPADÓW KUCHENNYCH

Abstract: The research concerned the possibility of vermicomposting organic wastes separated from kitchen residues. Vermicomposting was conducted with the presence of the earthworm *Eisenia fetida* (Sav.) in ecological boxes. The occurrence of a dipteran *(Sciaridae)* was reduced by the application of anti-dipteran preparations into the substrate (in environmentally safe doses recommended by the producers). The insecticides Nomolt 150S.C, Dimilin 25WP and Dar 2.5GR were used. The aim of the research was to determine the influence of these preparations on the rate of vermicomposting and on the characteristics of the vermicomposts produced by *E. fetida.* Over a period of 6 months, it was shown that a Dar 2.5GR preparation had the largest impact on the daily rate of vermicomposting. The vermicomposts produced with the addition of insecticides did not differ in content of nutritional elements for plants (nitrogen N-NO_3, calcium, assimilable phosphorus, potassium and magnesium) in comparison with the control vermicomposts. The qualities of the produced vermicomposts were as follows: pH in H_2O 5.9-6.2; salt concentration: min 4.7 - max 5.4 g NaCl · dm^{-3}, nitrogen N-NO_3 min 808 - max 902; phosphorus P min 344 - max 372; potassium K min 1185 - max 1424; magnesium Mg min 279 - max 335 mg · dm^{-3}; calcium Ca min 1940 - max 2381 mg · dm^{-3}.

Keywords: ecological boxes, *Eisenia fetida*, *Sciaridae,* insecticide, vermicompost

At present, many factors have an influence on the quality of the natural environment, with excessive contamination of xenobiotics as decisive factor in disturbing homeostasis and leading to deteriorating quality of crops [1]. Poorly utilized wastes, including organics, can also pose a threat. As a consequence, finding pro-environmental solutions to this problem is a matter of urgency [2]. One of the solutions might be to vermicompost the organic wastes (*eg* household wastes) in ecological boxes at the site, where they are produced. Such actions can ensure the utilization of segregated organic wastes and can also facilitate the production of vermicompost - a coprolithic fertilizer, rich in nutritional elements for plants [3-6].

Vermicomposting on a small scale in ecological boxes has some disadvantages such as the troublesome presence of dipterous insects, which compete with earthworms for food (the wastes). In order to eliminate this inconvenience, insecticides can be added to the wastes.

In this research, the ecological boxes contained anti-dipteran insecticides - phosphorganic Dar 2.5GR and two inhibitors of chitin biosynthesis, Dimilin 25WP and Nomolt150SC, in environmentally safe doses recommended by the producers. The influence of these insecticides on the daily rate of vermicomposting and on the characteristics of vermicomposts produced was examined in laboratory conditions.

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Materials and methods

The research was conducted in a climate chamber (in containers of size $21 \cdot 15 \cdot 10$ cm^3), in which constant humidity was maintained (approx. 70%), according to the norm [7], and the ambient temperature was 20°C. The stratification layer was substrates with the volume of 2 dm^3 and with characteristics shown in Table 1.

The following waste materials were vermicomposted: in each case 150 cm^3 of cooked pasta, bread, apple and potato peelings (600 cm^3 of waste in total), mixed with 300 cm^3 of shredded cellulose, added to improve the conditions of vermicomposting (shredded egg boxes) [3]. In order to check the possibility of utilization of insecticides which limit the occurrence of dipterous insects (*Sciaridae)* in the ecological box, the following preparations were added to the vermicomposted mass: Dimilin 25WP (dose of $4\ \text{g} \cdot \text{m}^{-2}$, active substance diflubenzuron), Nomolt 150SC (dose of $5\ \text{cm}^3 \cdot \text{m}^{-2}$, active substance teflubenzuron), and Dar 2.5GR (dose $400\ \text{g} \cdot \text{m}^{-2}$, active substance chlorfenvinfos).

Table 1

Plan of kitchen wastes vermicomposting

Containers	Insecticide*	Stratification layer	Vermicomposted waste	Earthworms
1-5	Control	In each case 2 dm^3 of universal medium for ornamental plants**	In each case 600 cm^3 of kitchen organic waste*** and 300 cm^3 of cellulose into each container	In each case 50 sexually mature specimens of *E. fetida* with a balanced total biomass (20.3 ± 0.6 g) into each container
6-10	Dimilin 25WP			
11-15	Nomolt 150SC			
16-20	Dar 2.5GR			

*in doses advised by the producer; **universal medium for ornamental plants Floro-hum: highmoor peat, lowmoor peat, pearlite, sand, microelements, mineral fertilizer NPK (pH in H_2O - 6.2; salinity - $0.5\ \text{mg} \cdot \text{dm}^{-3}$; $N\text{-}NO_3$ - $18\ \text{mg} \cdot \text{dm}^{-3}$; P - $63\ \text{mg} \cdot \text{dm}^{-3}$; K - $186\ \text{mg} \cdot \text{dm}^{-3}$; Mg - $141\ \text{mg} \cdot \text{dm}^{-3}$; Ca - $1027\ \text{mg} \cdot \text{dm}^{-3}$; ***in each case 150 cm^3 of cooked pasta and bread leftovers, apple and potato peelings mixed with cellulose in the ratio of 2:1

The average rate of vermicomposting the above-mentioned organic wastes was calculated thanks to their isolation from the stratification layer and then from the produced vermicompost, by placing them inside a large-holed nylon mesh (which simultaneously facilitated free access of the earthworms). The rate of waste processing into vermicompost was determined regularly (during inspection of the earthworm population in the control and treatment containers), by multiple comparison of the volume of the unprocessed wastes. The results obtained were compared with the volume of the leftovers processed into vermicompost according to the following formula:

$$a_t = 900 - b_t$$

where: a_t - the volume of processed leftovers in subsequent examinations b_t - the volume of subsequently determined leftovers (not processed by earthworms).

The characteristics of produced vermicomposts were determined in a dynamic system (three times). The content ($N\text{-}NO_3$, P, K and Mg and Ca) was determined in the extract of 0.03 moles of acetic acid CH_3COOH by means of the following methods: the content of nitrogen $N\text{-}NO_3$ potentiometrically with an ionometer and ion-selective electrode, phosphorus with the vanadium-molybdenum method, the content of potassium and calcium was determined by using a flame photometer and magnesium was checked with a spectrometer by means of atomic absorption (in mg · dm^{-3}). pH in water was determined potentiometrically and the concentration of salt conductometrically (in g NaCl dm^{-3}).

The results (presented as mean ± standard deviation, $n = 6$), were analysed by means of the spread sheet Excel. The calculated averages were compared by means of the variance method using the Tukey's t-test (the program Statistica PL was used).

Results and discussion

The research demonstrates the efficiency of vermicomposting of chosen kitchen leftovers on site where the waste is produced - in earthworm ecological boxes [6]. In the present research, special attention is paid to the influence of xenobiotics on the process of the monthly rate of vermicomposting. It transpired that only in the case of the acyl urea preparation - Dimilin 25WP - the efficient removal (from the substrate) of larvae of *Sciaridae* competing with earthworms for food (organic waste) affected the increase in the rate of processing waste into vermicompost (Table 2).

In contact with xenobiotics Dar 2.5GR and Nomolt 150SC, the rate of vermicomposting reduced. The lower rate of vermicomposting, in comparison with the control, was determined in the presence of Dar 2.5GR (significantly to control and Dimilin 25WP) and Nomolt 150SC (non-significantly).

Table 2

The influence of the tested preparations on the rate of vermicomposting of selected organic wastes [cm^3/day/ 1 dm^3 of vermiculture]

Tested preparation	**Control**	**Dimilin 25WP**	**Nomolt 150SC**	**Dar 2.5GR**
The volume of processed wastes	6.8±2	7.0±2	6.0±2	4.5±2
The volume in relation to the control [%]		102	88	66
p level				
Control		.999688	.863869	**.000336**
Dimilin 25WP	.999688		.859634	**.003370**
Nomolt 150 SC	.863869	.859634		.153583
Dar 2.5GR	**.000336**	**.003370**	.153583	

The daily rate of vermicomposting in control containers achieved in the experiment is in accordance with the data given by Sinha and others [8]. The vermicompost had a granular structure - with no remaining unprocessed wastes. Conducted under laboratory conditions, the vermicomposting proceeded smoothly, without emitting unpleasant smells (odourless). The range of pH values in the produced vermicomposts was 5.9÷6.2; they were not different as far as salt concentration was concerned, although this characteristic exceeded the tolerance threshold for garden plants - (up to 3 g NaCl · dm^{-3}). The produced vermicomposts were also not different with respect to the content of plant nutritional elements (nitrogen N-NO_3, assimilable phosphorus, potassium, magnesium and calcium) (Table 3).

The content of all the nutritional elements exceeded the optimal level for plants, which, in combination with the high salinity of the vermicomposts, indicates the absolute necessity for their dilution before use (Table 4).

Table 3

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

Tested preparation **Characteristic**	**Control**	**Dimilin 25WP**	**Nomolt 150SC**	**Dar 2.5GR**
pH in H_2O	5.9÷6.2	5.9÷6.0	5.9÷6.0	5.9÷6.2
The concentration of salt [g NaCl · dm^{-3}]	5.4±1.0	4.8±0.6	4.7±1.2	5.3±0.7
$N\text{-}NO_3$ [mg · dm^{-3}]	880±89	815±149	808±149	902±27
P [mg · dm^{-3}]	345±66	372±51	351±99	344±106
K [mg · dm^{-3}]	1415±198	1418±390	1285±253	1424±245
Ca [mg · dm^{-3}]	2124±356	1999±248	2241±249	2281±219
Mg [mg · dm^{-3}]	279±67	309±33	305±59	335±25

Table 4

Characteristics of vermicomposts obtained during research compared with optimal levels for plants

Characteristic	**pH in H_2O**	**Salinity NaCl [g · dm^{-3}]**	**Element [mg · dm^{-3} of fresh mass]**				
			$N\text{-}NO_3$	**P**	**K**	**Ca**	**Mg**
Produced vermicomposts	5.9÷6.2	4.7÷5.4	808÷902	344÷372	1285÷1424	1999÷2281	279÷335
The optimal level for garden plants*	6.0÷7.5	about 1.0	50÷120	40÷80	125÷250	1000÷2000	60÷120

*the optimal level for garden plants according to [9]

The production of vermicompost on site has invaluable ecological and economic importance, because it allows utilization of segregated organic wastes in a sensible way. An essential aspect in managing an ecological box is the permanent monitoring and control of the abiotic and biotic conditions of this process [3]. Vermicomposting should be performed according to specified steps, otherwise it will not proceed smoothly and odourlessly. For example, if proper humidity conditions are not provided (*eg* overflow in the substrate), anaerobic conditions can occur or an unpleasant smell can be emitted as a result of putrefaction beginning. The rate of processing wastes can, consequently, be reduced. The produced vermicomposts were rich in nutritional elements for plants and had pH in water close to neutral (min 5.9; max 6.2), although lower than that established by Kostecka in the vermicomposts from kitchen wastes [3], which, on average, was in the range of 6.5÷7.5. The characteristic feature of vermicomposts produced here was the high average concentration of salt (min - 4.7; max - 5.4 g NaCl · dm^{-3}). This fact confirms the earlier results of the research performed by Kiepas-Kokot and Szczech [10] and Kostecka [3], which determined a similar regularity and even higher values of this characteristic of vermicompost.

A high salinity of the substrate is an unfavourable factor for the proper growth of plants and that is why (in addition to the high content of nutritional elements for plants in the researched vermicomposts) before using this product for fertilization, all these values should be determined and dilution should be applied (appropriately for the species of the plant) [10-14]. As a result of the necessity of the limitation of the threat of higher concentration of salt in agricultural soils, it is also possible to mix the vermicomposted household wastes with cellulose, soil, peat or sand. It is a problem of utmost importance, because Kostecka [3] established that over the period of one year of farming, the salinity of fertilizers produced from household organic wastes rose from 3.9 to 12.6 g NaCl · dm^{-3}.

The conclusion that can be drawn from the present work is that the highest salinity of the substrate was the characteristic of vermicomposts in control (5.9÷6.2) and boxes with the preparations Dar 2.5GR (5.9÷6.2), and the lowest concentration of salt was found in the ecological boxes with the preparations Nomolt 150SC and Dimilin 25WP, although no statistically significant differences were determined. The average concentration of salt in the vermicomposts was at the level of 4.7 g NaCl · dm^{-3}.

During vermicomposting, earthworms permanently loosen the organic waste (thus producing a granular structure), which facilitates the development of the root system of plants after placing the vermicompost in soils. Earthworm excrements contain mucus, which facilitates the development of soil bacteria and also contain silica, available for plants and strengthening their cell walls. According to some authors, vermicompost, to a bigger extent than compost, stimulates the population growth of microorganisms [15, 16]. These animals also influence the accumulation of vitamin B_{12} in soil. After death, the tissues of the earthworm bodies, in which protein constitutes almost 70% of dry matter, rapidly decompose and become an additional source of nitrogen, which could easily become mineralized.

Conclusions

1. Organic kitchen waste can be neutralised on site - in earthworm ecological boxes. The troublesome presence of dipteran insects while managing the boxes can be minimised by means of the examined insecticides: Dimilin 25WP, Nomolt 150SC and Dar 2.5GR.
2. Among the tested anti-dipteran preparations, it is Dar 2.5GR that significantly reduced the daily rate of waste vermicomposting.
3. Vermicomposts produced from organic kitchen waste were rich in nutritional elements for plants (nitrogen $N\text{-}NO_3$, assimilable phosphorus, potassium and magnesium and calcium).
4. Because the salinity of vermicomposts from kitchen waste exceeded the tolerance threshold for plants, the produced fertilizers should be diluted before applying them in agricultural soils.

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WPŁYW WYBRANYCH INSEKTYCYDÓW NA CECHY WERMIKOMPOSTÓW WYPRODUKOWANYCH Z ODPADÓW KUCHENNYCH

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Abstrakt: Badania dotyczyły wermikompostowania segregowanych kuchennych odpadów organicznych w skrzynkach ekologicznych z zastosowaniem dżdżownic *E. fetida* (Sav.). Występowanie muchówek *Sciaridae* zredukowano w nich przez aplikację do podłoży preparatów antymuchówkowych (w dawce zalecanej przez producentów). Użyto insektycydów Nomolt 150SC, Dimilin 25WP i Dar 2.5GR. Celem badań było określenie wpływu tych preparatów na tempo wermikompostowania i na cechy wyprodukowanych przez *E. fetida* wermikompostów. Przez okres 6 miesięcy prowadzenia badań wykazano, że jedynie preparat Dar 2.5GR istotnie obniżył dzienne tempo wermikompostowania. Wyprodukowane wermikomposty z dodatkiem insektycydów nie różniły się zawartością składników pokarmowych roślin (azotu N-NO_3, przyswajalnego fosforu, potasu i magnezu oraz wapnia) w porównaniu do wermikompostów z pojemników kontrolnych. Cechy wyprodukowanych wermikompostów kształtowały się następująco: pH w H_2O 5,9÷6,2; stężenie soli min. 4,7, max 5,4 g NaCl $\cdot$ dm^{-3}, azot N-NO_3 min. 808, max 902; fosfor P min. 344, max 372; potas K min. 1185, max 1424; magnez Mg min. 279, max 335 mg $\cdot$ dm^{-3}; wapń Ca min. 1940, max 2381 mg $\cdot$ dm^{-3}.

Słowa kluczowe: skrzynki ekologiczne, *Eisenia fetida*, *Sciaridae,* insektycydy, wermikomposty

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ANTIFUNGAL ACTIVITY OF BACTERIAL SPECIES *Pseudomonas* AGAINST *Alternaria* sp.

AKTYWNOŚĆ PRZECIWGRZYBOWA BAKTERII Z RODZAJU *Pseudomonas* WOBEC *Alternaria* sp.

Abstract: The aim of the research was to determine a fungistatic activity of bacteria *Pseudomonas* against *Alternaria* sp. The antagonistic properties of metabolites were assessed with a culture-plate method on Czapek and PDA growth media for *Pseudomonas* sp. cultures after 4, 6, 8, 10 and 24 hours of culturing. The culturing process was conducted at 22°C for 14 days. The fungistatic activity of *Pseudomonas* sp. strains was determined against the growth rate index. As proved by the results obtained, the strain of *Alternaria* sp. under study showed sensitivity to supernatants of *Pseudomonas* sp. The linear growth of the mycelium of *Alternaria* sp. was inhibited most actively by *Pseudomonas* sp. strain BK1. The highest decrease, amounting 76%, in the value of the growth rate index was obtained after 10 hours of culturing on Czapek medium. In case of *Pseudomonas* sp. strain marked KF1, the highest reduction in the growth rate index was noted for the 24-hour culture on PDA medium and amounted to only 18%. Conducted research confirms fungistatic activity of *Pseudomonas* sp. strains against *Alternaria* sp. and proves that the growth inhibition of mycelium depends not only on the metabolites types produced by a specific bacterial strain but also on the length of culturing process.

Keywords: fungistatic activity, growth rate index, *Pseudomonas* sp., *Alternaria* sp.

Plant diseases caused by fungi such as *Alternaria* and *Fusarium* constitute the most numerous and the most significant group of diseases taking into account an economic aspect. In order to control them the fungicides are applied, which despite their efficiency and simplicity are not highly ranked in the process. First of all, the fungicides may be hazardous to consumers as their particles may remain on the plants. Moreover, the substances induce the development of pathogens' immunity to such chemicals and a reduction of harmless organisms. In addition, it is difficult and expensive to develop new and safe products. Therefore, there has been more and more interest in biological methods of plants protection [1]. Consequently, more popular have become biological substances based on non-pathogenic microorganisms, such as bacteria of *Pseudomonas* kind, which are of great interest to scientists looking for efficient strains to be used in the process. The special attention has been brought to: *P. fluorescens*, *P. aeruginosa, P. putida* and *P. pyrrocinia*. The strains show antifungal activity with varying degrees of antagonism. According to literature sources [2-4], bacteria possess the ability to synthesize different substances which are biologically active, *ie* hydrogen cyanide, siderophore, salicylic acid and lytic enzymes, proteases.

The aim of conducted research was to determine how metabolites produced by strains of *Pseudomonas* sp. KF1 and BK1 affect the growth of *Alternaria* sp.

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Materials and methods

For the experiment, test strains of *Pseudomonas* sp. marked KF1 and BK1 isolated from the natural environment were used together with an indicator strain *Alternaria* sp.

Fungistatic activity of tested strains was determined with the culture-plate method on Czapek medium consisting of [g/dm^3]: sucrose 30.0, $MgSO_4 \cdot 7H_2O$ 0.5, KH_2PO_4 1.0, KCl 0.5, $NaNO_3$ 3.0, $Fe_2(SO_4)_3 \cdot 7H_2O$ 0.01, agar 15.0 and on PDA medium consisting of [g/dm^3]: glucose 20.0, potato extract 4.0, agar 15.0. In bacterial cultures which were control trials, *Pseudomonas* sp. was added to the media as supernatants obtained after 4, 6, 8, 10 and 24 hours of culturing. Next, the media were inoculated with fungi discs of 10 mm diameter. The control trial contained *Alternaria* sp. cultures and aseptic broth medium in place of the supernatant. All plates were cultured at 22ºC for 14 days. After 2-4 days the diameters were measured until *Alternaria* sp. on the plate with the control trial grew over the whole surface of the plate. The experiment was conducted in three trials, where one trial was represented by one plate containing the growth medium with one mycelial disc.

The influence of metabolites produced by *Pseudomonas* sp. on the growth of *Alternaria* sp. was determined against the growth rate index, calculated according to the formula below [5]:

$$T = \frac{A}{D} + \frac{b_1}{d_1} + \frac{b_2}{d_2} + \ldots + \frac{b_x}{d_x}$$

where: T - growth rate index, A - mean value of diameter measurements [cm], D - the length of the experiment [number of days], b_1, b_2, b_x - increase in a diameter size since the last measurement, d_1, d_2, d_x - number of days since the last measurement.

Results

In the experiment, 2 bacterial strains *Pseudomonas* (KF1 and BK1) were tested against their ability to synthesize exocellular metabolites possessing fungistatic abilities in relation to *Alternaria* sp. On the basis of obtained results, it has been proved that fungistatic activity of tested *Pseudomonas* is varied and depends on the type of the growth medium and the length of culturing.

It has been observed, in conducted tests, that strain *Pseudomonas* KF1 was least active in terms of its fungistatic activity on PDA medium (Fig. 1). For the supernatants obtained after 6 and 8 hours of culturing, a decrease in the growth rate index has not been recorded in comparison with the control trial. As measured, the increase in the growth rate index amounted 3.48 and 7.15% respectively for the above. Only after having supplemented the growth medium with 4, 10 and 24-hour cultures, the drop of the growth rate index was noticeable and the reduction amounted between 2.72 and 18.17%. The linear growth of the mycelium was inhibited most actively when the supernatant of 24-hour culture was added to the growth medium.

The analysis of *Alternaria* sp. growth on Czapek medium with an addition of supernatants of *Pseudomonas* sp. KF1 revealed much more intensive drop of the growth rate index than on PDA (Fig. 2). The degree of obtained reduction, however, has not been high and amounted from 7.27% for the 6-hour cultures to 13.58% for the 24-hour culture.

In the control trials of *Alternaria* sp. the value of the growth rate index was raising with the length of culturing time and amounted 3.41 for 4-hour culture to obtain the value of 3.91 for 24-hour culture. Similar relationship has not been noted for *Alternaria* sp. growing on the medium with sucrose (*ie* Czapek medium).

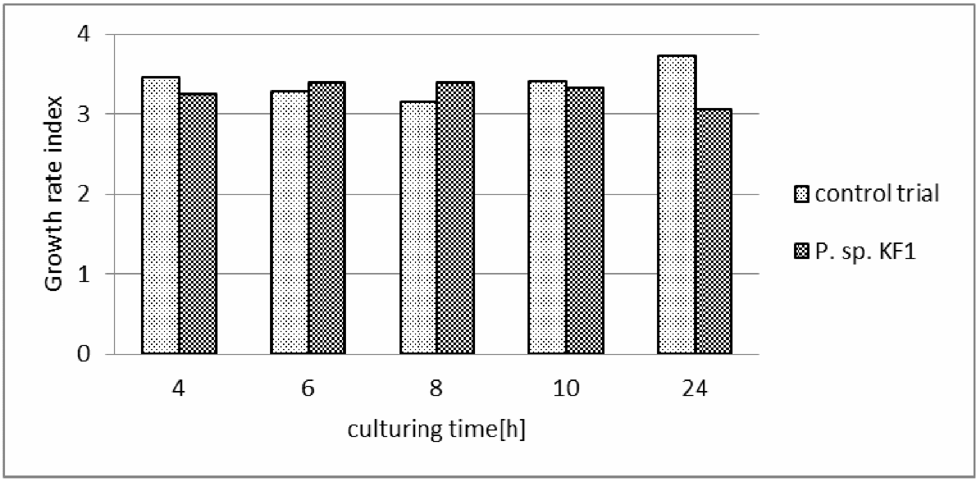

Fig. 1. The influence of *Pseudomonas* sp. KF1 on mycelial growth of *Alternatia* sp. on PDA medium

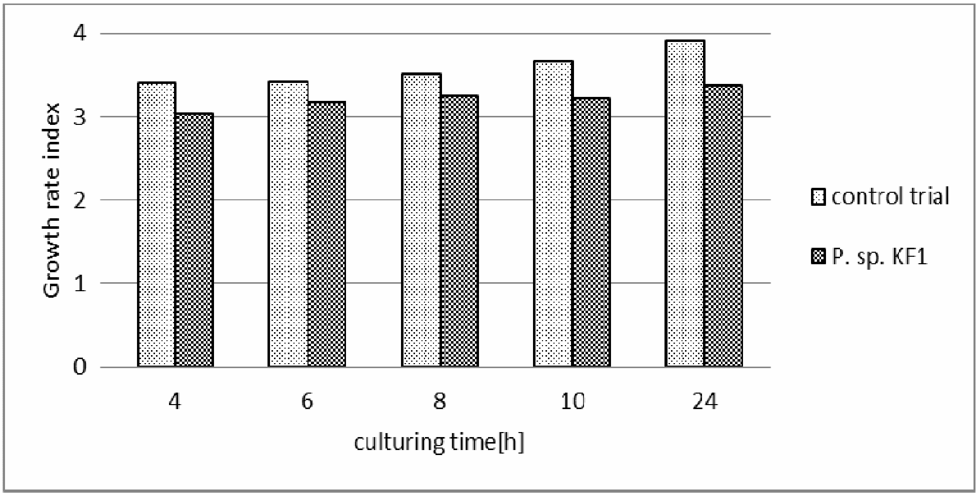

Fig. 2. The influence of *Pseudomonas* sp. KF1 on mycelial growth of *Alternaria* sp. on Czapek medium

In presented tests, fungistatic activity was also determined for strain *Pseudomonas* sp. BK1 against *Alternaria* sp. Consequently it has been revealed that supernatants obtained from 4-hour cultures caused significant inhibition of the linear growth of *Alternaria* sp. (Fig. 3) and measured value of the growth rate index reduction amounted 61.37% when compared with the control trial. Similar reduction has been recorded for 10-hour culture (61.92%). Both results were the highest recorded values for such bacteria-fungus combination. For the remaining trials, a lower reduction in the growth rate was recorded: 59% for 6-hour culture and 57% for 8-hour culture. An antagonistic activity of *Pseudomonas* sp. BK1 was least efficient when the supernatant was obtained after 24 hours of culturing. The value of the growth rate index was the lowest for both the control trial (2.25) and the particular trial (1.54) and the decrease of index amounted only 31.5%.

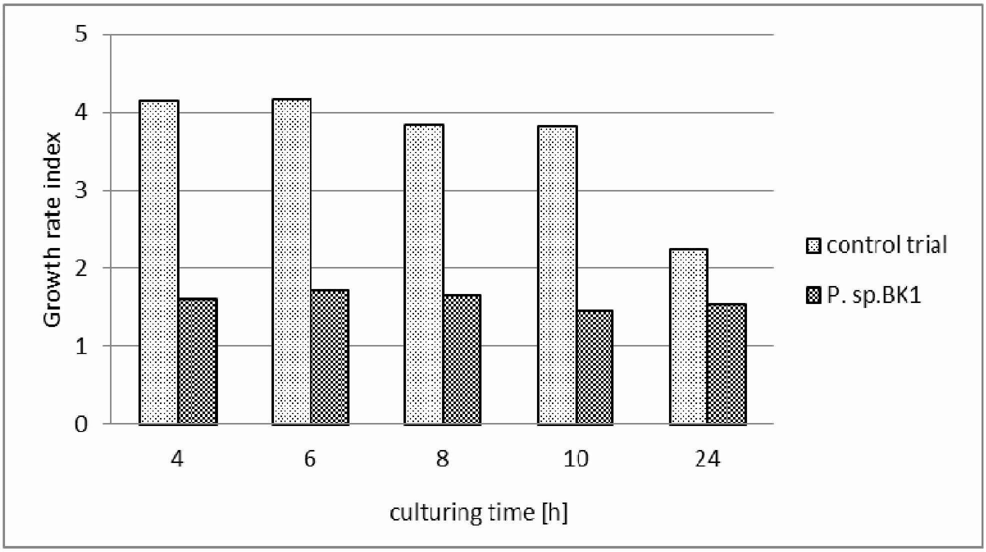

Fig. 3. The influence of *Pseudomonas* sp. BK1 on mycelial growth of *Alternaria* sp. on PDA medium

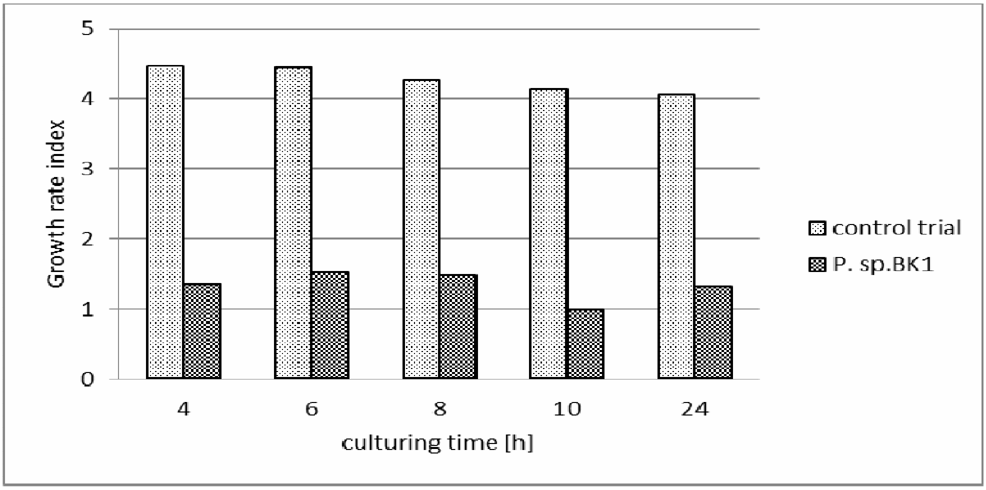

Fig. 4. The influence of *Pseudomonas* sp. BK1 on mycelial growth of *Alternaria* sp. on Czapek medium

On the basis of obtained results concerning the growth rate index it may be stated that strain *Alternaria* sp. showed the fastest linear growth on the medium with sucrose (Czapek medium) as showed in Figure 4. The plate was fully covered with the fungus only after 8 days of the experiment. The values of the growth rate index obtained in control trials were the highest throughout the whole experiment and fluctuated between 4.46 for 4-hour culture and 4.05 for 24-hour culture. At the same time, the value of the growth rate index in control trials was significantly lower and resulted in the highest reduction of the mycelial growth rate. It amounted to 76% in case of the supernatant obtained from 10-hour culture. The values obtained for other cultures were also high (65÷70%).

It is worth noticing that obtained values of the growth rate index for the control trials on Czapek medium were higher in comparison with the ones obtained on PDA medium. Therefore, in most cases, linear growth of mycelium was inhibited more actively on Czapek medium as noted for strains of *Pseudomonas* sp. KF1 and *Pseudomonas* sp. BK1. It may probably result from different sources of carbon in the growth medium (glucose or sucrose) and different preference towards them showed by tested strain of *Alternaria* sp.

Summary and conclusions

Conducted research showed significant diversity of fungistatic activity among particular *Pseudomonas* sp. strains. The growth of *Alternaria* sp. was inhibited most actively by the exocellular metabolites produced by *Pseudomonas* sp. BK1. The most optimal results have been obtained on Czapek medium with sucrose as carbon source. The lowest fungistatic activity was observed for *Pseudomonas* sp. KF1 and the growth medium for which the results were satisfactory was the growth medium with sucrose. However, the growth inhibition was so low when compared with the results obtained for *Pseudomonas* sp. BK1, that it seems unlikely to apply the strain to control *Alternaria* fungi.

Moreover, on the basis of obtained results, it shows that the most favourable is to apply 10-hour cultures to inhibit the linear growth of *Alternaria* sp.

To sum up, strains of *Pseudomonas* sp. may find a wide range of applications in the process of plant protection against diseases caused by *Alternaria* sp. However, the differences in fungistatic activity between tested strains, revealed in the experiment, may be the evidence that it is typical for a specific strain, which depends not only on the length of culturing time, but also on the type of the growth medium or the environment it is designed for.

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AKTYWNOŚĆ PRZECIWGRZYBOWA BAKTERII Z RODZAJU *Pseudomonas* WOBEC *Alternaria* sp.

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Abstrakt: Celem badań było określenie aktywności fungistatycznej bakterii z rodzaju *Pseudomonas* wobec *Alternaria* sp. Ocenę właściwości antagonistycznych metabolitów przeprowadzono metodą hodowlano-płytkową na podłożu Czapka oraz PDA dla 4-, 6-, 8-, 10- i 24-godzinnych hodowli *Pseudomonas* sp. Hodowlę prowadzono w temperaturze 22ºC przez 14 dni. Na podstawie indeksu tempa wzrostu określono aktywność fungistatyczną szczepów *Pseudomonas* sp. Wyniki doświadczenia wskazują, że badany szczep *Alternaria* sp. był wrażliwy na działanie supernatantów *Pseudomonas* sp. Największą inhibicję rozrostu liniowego grzybni *Alternaria* sp. powodował szczep *Pseudomonas* sp. BK1. W tym przypadku najwyższy 76% spadek indeksu tempa wzrostu grzybni uzyskano dla 10-godzinnej hodowli na podłożu Czapka. Natomiast dla szczepu *Pseudomonas* sp. KF1 największą redukcję indeksu tempa wzrostu odnotowano dla 24-godzinej hodowli na podłożu PDA, jednak wynosiła ona jedynie 18%. Przeprowadzone badania potwierdzają fungistatyczne działanie szczepów *Pseudomonas* sp. wobec *Alternaria* sp. Ponadto wykazują, że inhibicja wzrostu grzybni uzależniona jest nie tylko od rodzaju metabolitów wydzielanych przez dany szczep bakterii, ale również od wieku jej hodowli.

Słowa kluczowe: aktywność fungistatyczna, indeks tempa wzrostu, *Pseudomonas* sp., *Alternaria* sp.

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DIVERSITY OF NEEDLES OF THE SCOTS PINE (*Pinus sylvestris* L.)

ZRÓŻNICOWANIE IGLIWIA SOSNY ZWYCZAJNEJ (*Pinus sylvestris* L.)

Abstract: The size of needles is usually described by their mass and length. These parameters depend on many factors, mainly on the amount of available water, light and temperature. The literature provides only rudimentary data on the surface of needles. But the surface of needles determines the growth of tree biomass, including wood, the product of the economic importance. The study aimed to verify if the mass of the needles is a good parameter to determine efficiency of the production in an individual pine or in population of pines. The material used consisted of needles from 48 model trees, collected at 31 study sites. All sites represented the same habitat type (fresh mixed coniferous forest), but they differed in the density and the age of trees. The study was conducted in young tree stands, between eight and twenty years old. We did not find any relation between the mean length of the needles and the age of trees. The shortest needles were found in 8 years old stand, and the longest needles came from 9 years old forest. The largest surface of the assimilation apparatus was found in a 20 years old pine. This corresponds with the culmination of the individuals' vertical growth in Scots Pine. The largest mass of the needles, 21 kg of the fresh mass, was recorded in the same tree stand, as well as the smallest and the largest number of needles on a tree.

Keywords: assimilation apparatus, needles, Scots Pine

The size of needles is usually described by their mass and length [1-3]. These parameters depend on many factors, mainly on the amount of available water, light and temperature [4]. Studies on the Scots Pine showed that the mass and the length of the needles was the largest in the top verticiles, and decreased regularly towards the base of the canopy [2]. The length of the needles was very variable even within a tree canopy [4]. The length of needles differed considerably between shoots that grew during different growth seasons. It has not been finally determined whether the needles reach their maximum dimensions during one growth season or are they still able to grow during following years.

We observed variation in the mass of the needles related with their location within the tree canopy. Needless in the side of the canopy exposed to sun are usually thicker and have thicker skin with xeric features than the needles at the shaded side, which are smaller and contain more water than those from the sunny side.

The literature provides only rudimentary data on the surface of needles. But the surface of needles determines the growth of tree biomass, including wood, and is the product of the economic importance. The study was aimed to compare two methods, the first one using the mass of needles and the second using the surface of needles, to calculate the efficiency of the biomass production in the Scots Pine.

Materials and methods

The material used consisted of needles from 48 model trees, collected at 31 study sites. All sites represented the same habitat type (fresh mixed coniferous forest), but they differed

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in the density and the age of trees. The study was conducted in young tree stands, between eight and twenty years old.

Study plots were established the Opole county, in the Niemodlin and Stobrawa Forests. All trees at the study plots were marked with individual numbers. Model trees were selected according to the variation of their diameters (d_0 or $d_{1,3}$) so that they were representative for the whole population. These trees were cut down, their needles were collected, and 1000 pairs of needles were selected from each tree and weighed to determine the number of needles at a whole tree. Analogously, 200 pairs of needles were measured for each model tree, to identify the length of the needles.

Results

The study showed that there was no direct relation between the mass of all needles and the age of a tree. Figure 1 shows the fresh mass of needles from model trees in relation to the age of trees. A 20 years old pine had the largest mass of needles - 21.14 kg. But a tree of the lowest mass of needles, only 0.20 kg, was found in the same population.

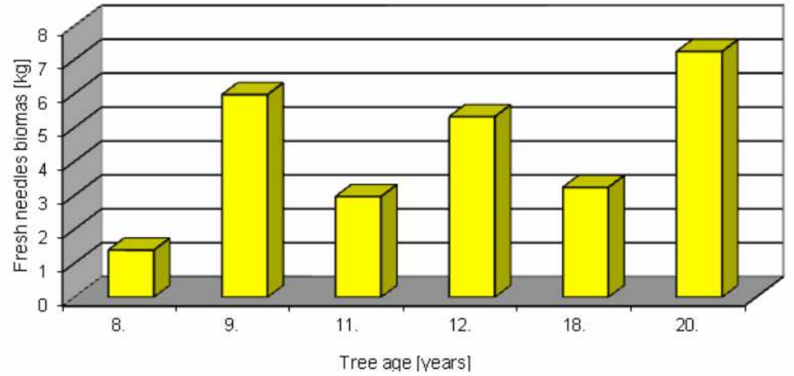

Fig. 1. The mean fresh mass of needles from model trees

Fig. 2. The mean fresh mass of 1000 pairs of needles

The mean mass of 1000 pairs of needles was not related with the age of trees. The fresh mass of 1000 pairs of needles was between 55 g and 90 g in the tree stands of different age (Fig. 2). The mean length of needles was also not correlated with the age of the trees (Fig. 3). The number of needles at each tree was calculated from the proportion of the mass of all the needles at a tree to the mass of 1000 pairs of needles (Table 1).

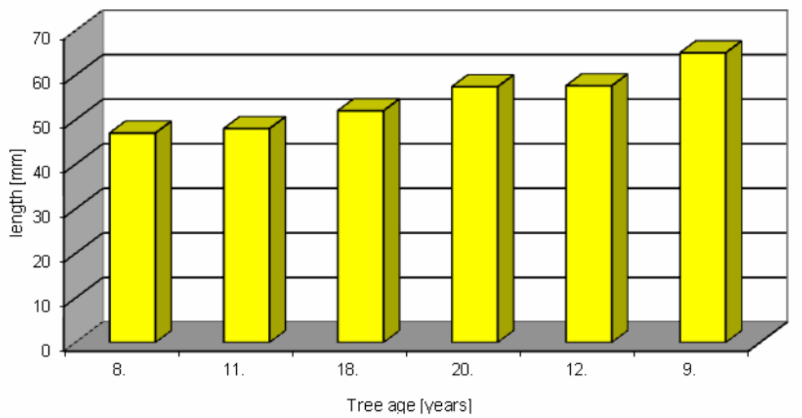

Fig. 3. The mean length of the needles

Table 1

The number of needles at the model tree

Tree age [years]	**The number of needles at the model tree**		
	Min	$\bar{x}$	**Max**
8	8901	24 075	46 861
9	1980	57 734	167 735
20	934	113 815	309 589

Knowing the surface of a needle of a given length and its mass we calculated the surface of all needles at each model tree. Having diameters of all the trees in a study plot and knowing the diameters of the model trees, we calculated the surface of needles if all trees in the study plot by interpolation. The 20 years old tree stand had the largest surface of needles (Table 2) [5].

Table 2

The surface of the assimilation apparatus

Stand age [years]	**The surface of the assimilation apparatus [m^2/ha]**	**Relative values**
8	37 318	0.30
11	65 955	0.53
18	89 953	0.73
20	123 399	1.0

The measurements of the length of needles, the number of pairs of needles in a tree canopy, the mass of 1000 pairs of needles and the mass of all needles at a tree, showed high variation of these features among trees of the same age and among the populations of Scots Pine of different age [5]. High inter-specific variability of the Scots Pine is the reason why pines of low and high mass of needles occurred next to each other. The density had a clear effect on the differences in the mass of the needles between pine populations of different age. Up to a certain level of competition between pines for resources required for life, individuals are not eliminated from the community but their size decreases and different features of the tree (stem, branches, needles) adapt to the density.

Analysing the relation between the growth of the biomass (Δm) and the mass of needles (m_l) in an individual tree, we noted that the increment increased with the increase of the mass of needles, but gradually slower. Because of the shade the lowest needles in the tree canopy are at the threshold of the natural compensation point, where the photosynthesis equals respiration within the 24-hours cycle. Thus these needles do not take part in the production of the wood biomass despite they enlarge the surface of the assimilation apparatus. This is because the needles from the upper part of the canopy shade the needles below, and this shading is the highest the largest is the mass of the needles. This probably affects the total production of the biomass.

Conclusions

1. The study showed that the assimilation surface of the needles provides a more accurate measure of the biomass production than the mass of the needles.
2. With the same mass of the needles, the photosynthetic surface can be up to four times higher with small needles, than with large needles.

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ZRÓŻNICOWANIE IGLIWIA SOSNY ZWYCZAJNEJ (*Pinus sylvestris* L.)

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Abstrakt: Wielkość szpilek charakteryzuje się najczęściej poprzez ich masę i długość, które zależą od wielu czynników, przede wszystkim od ilości wody, światła i temperatury. W literaturze przedmiotu znajdują się szczątkowe dane dotyczące pola powierzchni szpilek, które to decydują o przyroście biomasy, w tym drewna, czyli sortymentu ważnego z punktu widzenia gospodarczego. Celem badań było porównanie dwóch metod obliczeń wydajności produkcyjnej biomasy sosny zwyczajnej z ciężaru igliwia oraz z jego powierzchni. Materiał do badań stanowiło igliwie z 48 drzew modelowych pobranych z 31 stanowisk badawczych. Wszystkie powierzchnie reprezentowały ten sam typ siedliskowy (BMśw.), różniły się natomiast zagęszczeniem i wiekiem. Badania prowadzono w młodnikach, z których najmłodszy liczył 8 lat, a najstarszy 20 lat. Nie stwierdzono związku między średnią długością igieł a wiekiem drzew. Najkrótsze szpilki odnotowano w 8-letnim młodniku, najdłuższe 9-letnim. Największe pole aparatu asymilacyjnego miała 20-letnia sosna, co pokrywa się z kulminacyjnym przyrostem osobników na wysokość. W tym drzewostanie zarejestrowano również największą masę igliwia wynoszącą 21 kg (św.m.) oraz największą, a zarazem najmniejszą liczbę szpilek.

Słowa kluczowe: aparat asymilacyjny, igliwie, sosna zwyczajna

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INITIAL ASSESSMENT OF THE POWER GENERATION POTENTIAL OF SELECTED HYDROPOWER PLANTS IN THE DOLNOSLASKIE AND OPOLSKIE PROVINCES

WSTĘPNA OCENA POTENCJAŁU ENERGETYCZNEGO WYBRANYCH ELEKTROWNI WODNYCH W WOJEWÓDZTWACH DOLNOŚLĄSKIM I OPOLSKIM

Abstract: Arrangements made at the latest EU climate and energy summits as well as the Directive of the European Parliament and of the Council on the promotion of the use of energy from renewable sources set out the rules for how Poland is to achieve the 15% target of total primary energy from renewables by 2020. The share of RES in national energy consumption (150 TWh) is estimated at 8.6 TWh in 2009 (5.7%) and 12 TWh in 2011 (8%). The authors studied selected rivers in the Dolnoslaskie and Opolskie provinces in terms of their capability for hydropower generation. To this end, locations were identified on the Odra, Nysa Klodzka and Nysa Luzycka, in which hydropower plants might be built or opened. Calculations indicate that the total theoretical power capacity of proposed power plant locations and the average energy of investigated watercourses stand at about 21.653 MW and 189.6 GWh/year, respectively. In view of the requirement of promoting the use of RES, the authors propose to carry out a comprehensive study and to calculate the hydraulic parameters and/or hydropower indicators for all the watercourses located in the Dolnoslaskie and Opolskie provinces.

Keywords: renewable energy sources, watercourse power and energy

Today we are witnessing a strong interest in *Renewable Energy Sources* (RES), which comes in the context of environmental protection and climate change on the Earth [1-3]. According to ESHA (*European Small Hydropower Association*), Poland makes use of only 17% of its technical potential for hydropower generation, whereas the European average is around 50% [4, 5]. During the latest energy summits in Brussels a decision was taken that Europe must increase the share of RES in its overall energy balance. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources sets out the rules for how Poland is to achieve the 15% share of renewables in the total of primary energy generated in 2020. The National Action Plan expresses concerns that the targets of this Directive may not be met. These fears are confirmed by the computation of *renewable energy* (RE) share in the national electricity consumption over the last several years. In 2009, the share of RE stood at 5.7% and rose to 8% in 2011 [6].

As of today, the fundamental and strategic EU document on energy is the "Communication from the Commission to the European Council and the European Parliament - an energy policy for Europe", which is part of the so called "Energy package" of January 2007. The ambitious targets set out for 2020 are as follows: a 20% reduction of greenhouse gas emission (compared with the 1990 level), a 20% reduction of primary

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energy consumption and a 20% share of primary energy from RES. These goals are differentiated for each EU member state according to its unique infrastructure characteristics, resources and achievements so far. As an important element of the "Energy policy", the action plan or the so called "Roadmap" identifies *small hydropower* (SHP) as an important energy source in the electrical power generation system. The "Roadmap" supplements the document of the Commission in the area of renewable power generation. It reveals that the development of hydropower generation in Europe is slow. The annual growth of hydropower in the 2020-horizon is approximately 0.8% and decreases steadily. Compared to other RES *ie* wind, photovoltaic energy, biomass and geothermics, hydropower comes out poorly - the annual growth for the above-mentioned sources is 8.5, 20.6, 7.2 and 7.2%, respectively. On the other hand, however, small hydropower generation helps to reduce the greenhouse gas emission, makes use of renewable resources and is efficient in terms of the cost/results ratio. A comparison between the emissions of CO_2, NO_2 and SO_2 (in Mg) by small energy sources (up to 1 MW) for various types of fuel *ie* coal, natural gas, oil derivatives and hydropower proves that for an installed capacity of 4500 h/a hydropower is the only one with a zero emission level of all of the above-mentioned gases. All other fuels produce from 2250 to 3750 Mg of CO_2, from 0.6 to 3.7 Mg of NO_2 and from 0.02 to 4.6 Mg of SO_2 [7, 8].

A fundamental non-technical problem affecting the hydropower plants (and particularly the small ones) is the granting of authorizations, concessions and approvals. Recent data demonstrate that the average time required for the administrative procedure in Europe ranges from 1 year (Austria) to 12 years (Portugal). In Poland the procedure may take as long as 8 years.

An analysis of electric power generation in hydropower plants in Poland reveals that until 2007 the share of plants with a capacity exceeding 10 MW was greater than that of plants with capacities below 10 MW: large facilities generated 60% of the overall output of all hydropower plants in total.

Hydropower engineering in Poland and Europe - overview

When analysing the development of hydropower engineering, one must differentiate between the so called large and small hydropower plants. The difference between those two lies in the installed capacity. In Europe the upper limit for a SHP installed capacity may vary: 1.5 MW in Luxemburg and Sweden, 5.0 MW in Poland, Austria, Greece, the Netherlands and Germany and 10 MW in Belgium, Spain, Ireland and Portugal.

Water in Poland is scarce. The average annual rainfall is about 600 mm, and our surface water resources are in short supply. The existing reservoirs can store only about 5% of water.

Small hydropower plants are important both in the environment and in economy. SHPs:

- generate clean energy,
- play an important role in environmental protection,
- create a system of reservoirs and increase the so called small retention,
- are beneficial for the electrical power grid.

SHPs in Poland are currently divided into three groups:

- micro hydropower plants with a capacity of up to 300 kW,
- mini hydropower plants with capacities ranging from 301 to 1000 kW,
- small hydropower plants with capacities ranging from 1001 to 5000 kW.

Methods and research

The authors have studied the available materials and carried out a series of measurements for the selected watercourses in the Dolnoslaskie and Opolskie provinces, namely for the rivers Odra, Nysa Klodzka and Nysa Luzycka. These tasks included: inventorying the river bed condition, inventorying the damming structures and measuring the water levels and flow rates.

A summary of selected characteristics of these rivers is given in Table 1.

Table 1

Characteristics of investigated watercourses in the Dolnoslaskie and Opolskie provinces

River	**River length [km]**	**Catchment area [km^2]**		**The Odra river km at the river mouth**
		In total	**In Poland**	
Nysa Klodzka	181.7	4565.7	3744.5	181.3
Nysa Luzycka	251.8	4297.0	2196.7	542.4
The Odra river basin up to the Nysa Luzycka mouth	634.8	51703.7	43150.7	-

Table 2

Characteristics of proposed hydropower plant locations on the selected rivers in the catchment of the upper and middle reaches of the Odra

No.	**River name**	**River [km]**	**Head H [m]**	**Average flow Q_{av} [m^{3}s^{-1}]**
1	Odra	95.6, Kozle	2.61	79.2
2	Odra	0.96, Kozle (channel)	2.61	15.0
3	Odra	150.5, Opole	2.10	82.0
4	Odra	0.26, Opole (channel)	0.85	16.5
5	Odra	1.42 Opole (channel)	1.25	16.5
6	Odra	198.4, Brzeg	3.41	139.0
7	Odra	198.7, Brzeg	3.27	139.0
8	Odra	4.87, Wroclaw-Zacisze	2.30	29.5
9	Odra	5.15, Wroclaw-Rozanka	2.30	29.5
10	Odra	0.1, Wroclaw-Szczytniki	2.05	29.5
11	Odra	2.9, Wroclaw-Psie Pole	1.35	29.5
12	Nysa Klodzka	13.830	1.8	38.2
13	Nysa Klodzka	22.090	3.13	37.1
14	Nysa Klodzka	49.140	3.70	37.1
15	Nysa Klodzka	111.710	3.5	18.5
16	Nysa Klodzka	126.000	1.7	15.0
17	Nysa Luzycka	109.080	1.5	22.0
18	Nysa Luzycka	151.650	3.06	21.1
19	Nysa Luzycka	159.850	2.10	20.5
20	Nysa Luzycka	173.965	2.5	14.8

The authors have made an inventory of the river Odra, which also included its left tributaries (the Nysa Klodzka and the Nysa Luzycka) in the Dolnoslaskie and Opolskie provinces. Our focus was on the possible locations in which hydropower plants might be built. In order to assess the possibilities of hydropower generation, the following have been analysed:

- 34 damming structures on the Odra river,
- 15 damming structures on the Nysa Klodzka river,
- 27 damming structures on the Nysa Luzycka river.

The hydraulic heads of the structures listed below range from several dozen centimetres (sills, barrages) to several meters (weirs, dams).

Amongst the surveyed locations, in which damming structures could be built, 20 locations were identified where small hydropower plants with given capacities could be built or reconstructed. These 20 locations were eventually selected based on detailed analyses and were marked on topographic maps. Table 2 gives a summary of these locations combined with their hydrological characteristics, *ie* the head and the average flow Q_{av}.

Results and discussion

The theoretical power of the investigated watercourse N_{av} [kW] is given by:

$$N_{av} = 9.81 Q_{av} H_{av}$$

where: Q_{av} - flow averaged over a long enough time (several years) [$\mathrm{m^3s^{-1}}$] [9, 10], H_{av} - head (height difference) over the river reach [m].

Table 3

Theoretical power N_{av} and energy E_{av} for the proposed locations on selected rivers in the Dolnoslaskie and Opolskie provinces

No.	River name	Power N_{av} [kW]	Energy E_a [GWh/year]
1	Odra	2028	17.8
2	Odra	384	3.4
3	Odra	1689	14.8
4	Odra	138	1.2
5	Odra	202	1.8
6	Odra	4650	40.7
7	Odra	4459	39.0
8	Odra	666	5.8
9	Odra	666	5.8
10	Odra	593	5.2
11	Odra	391	3.4
12	Nysa Klodzka	674	5.9
13	Nysa Klodzka	1139	10.0
14	Nysa Klodzka	1347	11.8
15	Nysa Klodzka	635	5.6
16	Nysa Klodzka	250	2.2
17	Nysa Luzycka	324	2.8
18	Nysa Luzycka	633	5.5
19	Nysa Luzycka	422	3.7
20	Nysa Luzycka	363	3.2

The theoretical average energy E_{av} [kWh] obtained for the investigated river reach is given by [11]:

$$E_{av} = 8760 N_{av}$$

$$N_{av} = 9.81 H_t Q_{Et} \sum \eta$$

where: $\Sigma\eta$ - the product of efficiencies of individual components *ie* turbine η_t, gear η_g, generator and block transformer η_{tr}. These efficiency values are as follows: $\eta_t = 0.88 \div 0.93$; $\eta_g = 0.95 \div 0.98$ and $\eta_{tr} = 0.97 \div 0.995$. As a result, the product of all the above efficiencies is estimated at 0.84÷0.90.

The power output in kWh and the installed capacity in kW of each power plant have been initially estimated based on the available basic hydrological data.

Table 3 summarises the theoretical energy and power values for the rivers investigated in this study. Calculations show that the overall power N_{av} and energy E_{av} for the investigated locations are 21.6 MW and 189.6 GWh/year, respectively.

Conclusions

The authors have carried out a thorough investigation and analysis of the rivers flowing through the Dolnoslaskie and Opolskie provinces: the rivers Odra, Nysa Klodzka and Nysa Luzycka. Based on the adopted criterion (hydraulic head), 20 hydrostructures (weirs, dams, barrages, sills) have been identified on these rivers.

Inventorying and measurements of the above-mentioned watercourses show that there is a potential for hydropower generation on 20 cross-section in the catchment of the rivers under study.

It has also been concluded that the hydrological parameters of most of the identified locations for possible hydropower plants in the Dolnoslaskie and Opolskie provinces allow for power generation ranging from several hundred kW to a few MW.

Amongst the rivers under analysis in the Dolnoslaskie and Opolskie provinces, the greatest potential for hydropower generation is on the Odra river. The total theoretical capacity for the Odra is 15.9 MW, and the average power generation is approx. 139 GWh/year. In the case of the Nysa Klodzka and the Nysa Luzycka, the capacity and power generation stand at 4.1 MW, 35.5 GWh/year and 1.7 MW, 15.2 GWh/year, respectively.

In order to assess the exact hydropower parameters of all the watercourses in the Dolnoslaskie and Opolskie provinces, the authors propose to carry out a thorough study and hydrological measurements.

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WSTĘPNA OCENA POTENCJAŁU ENERGETYCZNEGO WYBRANYCH ELEKTROWNI WODNYCH W WOJEWÓDZTWACH DOLNOŚLĄSKIM I OPOLSKIM

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Abstrakt: Ustalenia z ostatnich szczytów klimatyczno-energetycznych UE oraz Dyrektywa Parlamentu Europejskiego i Rady z 2009 r. w sprawie promowania stosowania energii ze źródeł odnawialnych określają zasady dojścia przez Polskę w 2020 r. do 15% udziału tej energii w całej energii pierwotnej. Udział energii elektrycznej odnawialnej w krajowym zużyciu energii (150 TWh) wynosił: 8,6 TWh w roku 2009 (5,7%) oraz 12 TWh w 2011 roku (8%). Autorzy przebadali wybrane rzeki województw dolnośląskiego i opolskiego w aspekcie ich hydroenergetycznego wykorzystania. W tym celu wytypowano lokalizacje na Odrze, Nysie Kłodzkiej i Nysie Łużyckiej, gdzie można wybudować lub odtworzyć elektrownie wodne. Z obliczeń wynika, że dla proponowanych lokalizacji pod elektrownie sumaryczna moc teoretyczna i energia średnia dla rozpatrywanych cieków będą na poziomie 21,653 MW i 189,6 GWh/rok. W aspekcie wymogów promowania odnawialnych źródeł energii (OZE) autorzy proponują przeprowadzenie kompleksowych badań i obliczeń hydrologicznych parametrów hydroenergetycznych dla wszystkich cieków zlokalizowanych w województwach dolnośląskim i opolskim.

Słowa kluczowe: odnawialne źródła energii, moc i energia cieku

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PRELIMINARY RESULTS OF STUDIES ON RADIOISOTOPES ACTIVITY CONCENTRATIONS IN VICINITY OF CEMENT WORKS

WSTĘPNE WYNIKI BADAŃ AKTYWNOŚCI RADIOIZOTOPÓW W SĄSIEDZTWIE CEMENTOWNI

Abstract: In many cities the abandoned industrial estates can be found. Even if such area has been recultivated and prepared the regions located further from the historical source of pollution could not have been restored. In such areas some unwanted substances, originated from former industry, still remain in soil. Among others, the radioactive isotopes in significant concentrations could appear in processing of mineral materials as well as in branches of production where coal combustion is utilized. Soil samples were collected in the area of the former cement plant "Piast", situated within Opole city borders and in the area of nearby allotment gardens. A number of naturally occurring radioisotopes were found as well as artificial ^{137}Cs. The biggest radioactivity concentration was produced by ^{40}K and ^{137}Cs. Concentration of activities of the remaining radioisotopes was lower and similar to each other. No significant differences in activities of radionuclides in soil samples collected in former industrial estate and in allotment gardens were found.

Keywords: industrial pollution, radioisotopes, contamination

Within urban area limits different production plants can be found. They usually emit different pollutants, characteristic for factory and production type. First of all, activity of a plant as local and long distance pollution source is related to technologies used in production. Contemporary, emissions of pollution by a production plant is usually meticulously controlled and continuously monitored. In past such inspections were often not rigorous or were absent at all. As a result a number of harmful or burdensome substances appeared in surrounding of a plant.

In many cities the abandoned industrial estates can be found. Even if such area has been recultivated and prepared *eg* for human inhabitance or for recreation purposes, the regions located further from the historical source of pollution could not have been restored. It could be expected that some unwanted substances, originated from former industry, still remain in soil of the areas located in vicinity of production plants. Among others, the radioactive isotopes in significant concentrations could appear in processing of mineral materials as well as in branches of production where coal combustion is utilized.

Investigations of radioactive isotopes activity concentrations in soil are very important part of monitoring of population exposure to ionizing radiation. The absorbed dose is substantially affected by the natural radioactive isotopes contained in the soil. Also burning coal can release into the atmosphere large amounts of dust containing naturally occurring radionuclides such as uranium, radium, thorium and their decay products [1-3]. As a result contamination level of the environment depends on the content of radionuclide in

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combusted fuel [2-6]. Therefore, it is reasonable to conduct measurements of gamma radioactive isotopes near industrial plants, both the active and inactive ones.

Materials and methods

Soil samples were collected in the area of the former cement plant "Piast", situated in southeastern part of Opole. After over 70 years of cement production this plant was closed in 1978. In the distance of few hundred meters in south direction from industrial area, the allotment gardens are situated. In Figure 1 position of former "Piast" cement works (marked by letter A) and allotment gardens (marked by letter B) are shown. From these areas soil samples were collected, six from each place. Activity concentrations of radioisotopes were determined by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution. Geometry of samples container was Marinelli, and measuring process and analysis of spectra were computer controlled with use of the software GENIE 2000. The radiation spectrum was recorded day and night.

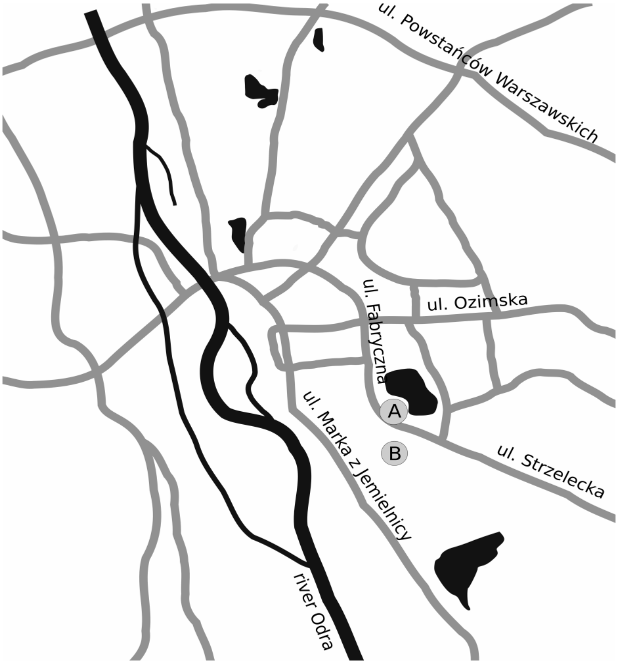

Fig. 1. Plan of Opole shown as scheme of main streets (gray color) in the city. Water reservoirs, river and channels are shown in black. Localization of former "Piast" cement works is marked with letter A, while letter B shows position of allotment gardens

Results

Distributions of radionuclides concentrations of activities are shown in Figure 2. The biggest activities were observed for naturally occurring ^{40}K and for the artificial isotope ^{137}Cs.

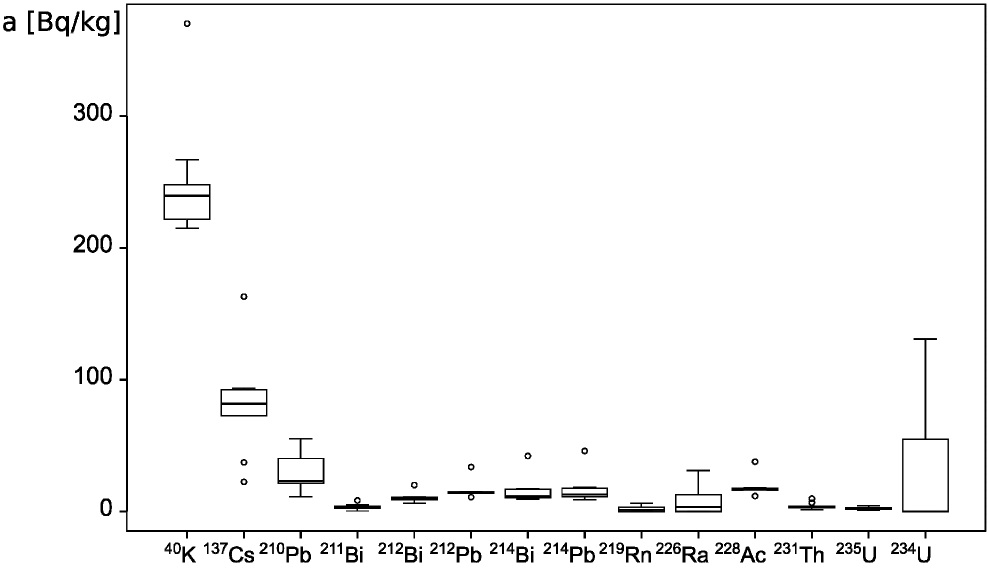

Fig. 2. Distributions of concentrations activities of radionuclides

Activity concentrations of the remaining isotopes were lower, and they were similar to each other.

In Figure 3 distributions of concentration activities in different places are compared. Distribution of isotope activities in samples collected in allotment gardens are marked by AG and distribution of the same parameter measured in samples from industrial estate are marked by P.

It can be noticed that medians of data are similar for all radionuclides. To compare concentration activities of radionuclides in soil in regions AG and P the Mann-Whitney-Wilcoxon test was used. This test enables assessing whether one of two samples of independent observations tends to have larger values than the other. It was found that on the p-level = 0.05 the measurement results obtained from AG and P can be regarded as originating from the same population.

Conclusions

Soil samples collected in the investigated areas contained a number of radionuclides. Most of them were of natural origin, only ^{137}Cs was artificial. Main sources of gamma radiation in soil were ^{40}K and ^{137}Cs. It was found that radioisotope composition of soils in industrial and non-industrial areas were similar. Some explanations can be supposed:

- activity of cement plant did not change composition of soil in both areas,
- range of pollution displacement was big enough to uniformly cover both areas,
- equalization of compositions is due to a long time of cement works inactivity.

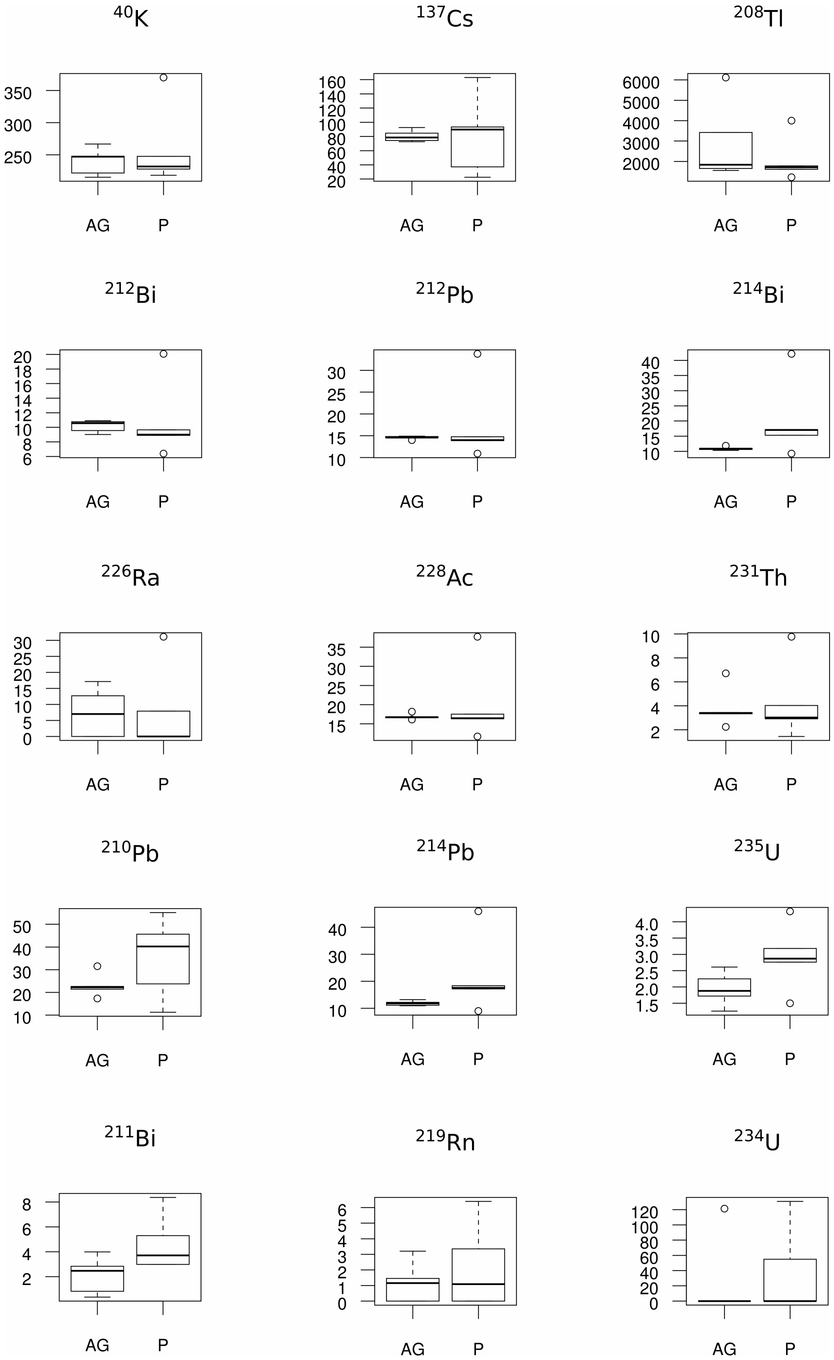

Fig. 3. Distributions of concentration activities in different places

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WSTĘPNE WYNIKI BADAŃ AKTYWNOŚCI RADIOIZOTOPÓW W SĄSIEDZTWIE CEMENTOWNI

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Abstrakt: W wielu miejscowościach znajdują się pozostałości po zakładach przemysłowych. Nawet jeśli taki teren został zrekultywowany, często obszary położone nieco dalej nie zostały przywrócone do pierwotnego stanu. Na takich terenach można spodziewać się istnienia podwyższonych stężeń różnych pierwiastków, w tym izotopów promieniotwórczych. Do badań pobrano próbki gleby na obszarze byłej cementowni „Piast", znajdującej się w granicach miasta Opola oraz na obszarze pobliskich ogródków działkowych. W badanych próbkach stwierdzono obecność naturalnych izotopów promieniotwórczych oraz ^{137}Cs. Największe aktywności wykazywały ^{40}K oraz ^{137}Cs. Aktywności naturalnych izotopów promieniotwórczych były znacznie niższe i porównywalne względem siebie. Nie stwierdzono istotnych różnic aktywności radionuklidów w próbkach gleby zebranych na obszarze byłych terenów przemysłowych oraz tych, które zebrano w ogrodach działkowych.

Słowa kluczowe: zanieczyszczenia przemysłowe, radioizotopy, skażenie gleby