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and Edita BALTRĖNAITĖ[1*]

RESEARCH AND ASSESSMENT OF BIOGAS EVOLVED DURING ANAEROBIC DIGESTION OF BIODEGRADABLE AGRICULTURAL WASTE

BADANIA I OCENA SKŁADU CHEMICZNEGO BIOGAZU Z ODPADÓW ROLNICZYCH PODCZAS FERMENTACJI MEZOFILNEJ W WARUNKACH BEZTLENOWYCH

Abstract: One of the methods for managing biodegradable waste generating in the Lithuanian agriculture is its anaerobic digestion in a bioreactor. This way of management would allow the recovery of biogas that can be used as an alternative to natural gas. The article analyses agricultural biodegradable waste and its use for the production of biogas in bioreactors. There were performed investigations through anaerobic digestion of pig manure (PM), hen manure (HM) and cow manure (CM) together with green waste biomass (GW) (GW accounted for 1, 2 or 5% of manure of the dry mass). GW is used to improve the ratio of nitrogen and carbon in the substrate (the optimal C:N is 25:1) which predetermines the composition and yield of released biogas. Before the experiment the substrate was prepared so as the dry matter in its content accounted for 10% of the total mass. Investigations were carried out in mesophilic conditions (t = 35 ±1°C). There were performed measurements of the yield of evolved biogas and methane, oxygen and sulphur hydrogen in it.

Keywords: biogas, agricultural biodegradable waste, methane, anaerobic digestion, bioreactor

Introduction

An economic crisis that emerged in Western Europe and USA 37 years ago (1973), having led to a continuous rise in the prices of fossil energy resources, particularly of oil and natural gas, accelerated search for alternative energy resources and studies on the possibilities of their use. Then, scientists and business people focused on biomass (wood, reed, sea vegetation, grain cultures, etc.) [1]. Currently the fossil fuel accounts for around 88% of the global energy demand [2].

During these days with the prices of fossil resources continuing to grow and an increasing focus being laid on waste management, one of the most promising methods of

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waste handling aimed at transforming organic waste into alternative energy and reducing access of organic waste to landfills as well as obtaining fertilisers, is anaerobic waste digestion in bioreactors [3, 4]. Furthermore, due to a significant rise in fossil fuel prices, an increasing amount of biofuel is produced from cultivated plants. A growing production of biofuel from cultivated plants has a negative effect on food prices and therefore scientific research on alternative energy production is becoming more and more important [5].

Anaerobic treatment of organic waste treatment is applied in farmers' farms, urban wastewater treatment plants, landfills, and food, light industry, bioethanol and biodiesel enterprises. The anaerobic method is used to treat animal and poultry manure, the organic part of municipal waste, sewage sludge from residential areas, wastes from food industry. The anaerobic treatment and use of organic waste for energy recovery is encouraged by increasingly stringent requirements related to environment protection, increasing costs of waste utilisation and growing prices of energy resources [6].

Apart from that, biological of organic waste results in the evolvement of gas with the prevailing amounts of methane (50÷70%) and carbon dioxide in it. Both methane and carbon dioxide are gases that cause the greenhouse effect [7, 8].

Methane is the main and most valuable component of biogas. If methane account for more than 60%, biogas is considered to be a valuable fuel [9, 10]. Beside biogas consists of NH_4, CO_2 and H_2O, also N_2, H_2S and O_2.

The use of biogas for heat and electricity production in a co-generation plant would significantly reduce methane emissions from agricultural biodegradable waste. Waste digestion in a bioreactor and the use of the recovered biogas for heat and electricity production instead of fossil fuel would also reduce CO_2 emissions in the Lithuanian energy sector. Furthermore, the use of biogas for energy recovery could be an additional source of income for farmers.

Raw materials for biogas production

Various types of biomass containing carbohydrates, proteins, fats and cellulose can be used for the production of biogas [11]. Livestock manure, plant residues, waste from the food industry and agriculture, sewage sludge, organic municipal waste, waste from public catering establishments, including energy plants, are suitable for biogas production. Biogas can also be collected from landfills by special devices.

The main flows of biodegradable waste generated by industrial and other activities accumulate in agriculture, food industry enterprises and wastewater treatment plants. It should be noted that agricultural biodegradable waste accounts for 80% of the country's biodegradable waste [2].

The main part of agricultural organic waste accumulates in cattle farms. In many cases subsidiary shops-slaughterhouses for the processing of production are equipped near major cattle farms. Therefore, apart from manure, these farms generate slaughter-house waste which is also suitable for the production of biogas and is used as an additive to enhance the output of biogas.

As many small-sized farms do not keep records of generating manure amounts, the quantities of manure are calculated in accordance with the number of livestock and poultry that are kept on these farms. On the basis of the data of a survey conducted in 2009, almost all slurry is applied as an organic fertiliser on farmers' or agricultural companies' fields. The amounts of manure accumulating in the Lithuanian agriculture are presented in Table 1.

Table 1

Manure amounts generating in the Lithuanian agriculture, 2009 [12]

Animal type	Amount of animals, in thou.	Manure yield (from an animal) [Mg/year]	Manure amount [thou. Mg/year]
Cattle	800.3	14.8	11840
Pigs	1114.7	1.7	1895
Poultry	9397.1	0.025	235
Total			13970

Biogas formation process, composition and properties

Biogas, like natural gas, consists of methane (CH_4) and carbon dioxide (CO_2) which is suitable for gas-stoves and heating boilers [13]. In order to improve the quality of biogas, it is necessary to remove CO_2 which generally accounts for 30÷45% in biogas and less than 1% in natural gas, as well as other impurities, particularly H_2S. After biogas is cleaned, it can be used by internal combustion engines of cars. Biogas is an effective natural gas, so emissions released by vehicles which use biogas are similar to those of vehicles using natural gas. However, the use of biogas causes lesser pollution of the environment as it is a renewable fuel and when burning emits a carbon amount similar to that it has absorbed from the atmosphere. The use of biogas also ensures that methane (gas causing the greenhouse effect) generating in agriculture is retained but not emitted into the atmosphere.

The use of biogas in cattle farms reduces expenditure on heat and power. The ratio of the main components of biogas, CH_4 and CO_2, depends on the primary composition of the substrate and the properties of the fermentation process (temperature, duration of preservation and work load of the bioreactor). Biogas also contains small quantities of H_2, N_2 and H_2S (Table 2).

The calorific value of biogas varies from 5000 to 7000 kcal/m^3 and depends on the concentration of CH_4 in it. For comparison, one cubic metre of biogas is equal to 0.7 m^3 of natural gas, 0.7 kg of fuel oil, 0.6 kg of kerosene, 0.4 kg of petrol, 3.5 kg of wood, 12 kg of manure briquettes, 4 kWh of electrical energy, 0.5 kg of carbon and 0.43 kg of butane [14].

Table 2

The main properties of biogas and its components [15]

Property and measurement unit	Components				Biogas (60% CH_4+40% CO_2)
	CH_4	CO_2	H_2	H_2S	
Theoretical content	55÷70	30÷45	< 1	< 3	100
Calorific value [MJ/m^3]	37.7	-	10.8	22.8	22.6
Flash point [ºC]	650÷750	-	530÷590	290÷487	650÷750
Lower explosive limits [%]	5÷15	-	4÷74	4÷42	6÷12
Density [kg/m^3]	0.72	1.98	0,09	1.54	1.2
Critical temperature [ºC]	–82.5	31.0	-	100	–82.5
Critical pressure [MPa]	4.6	7.3	1.3	8.9	7.3÷8.9

Biogas has been used in practice for many years already. Production of biogas from organic waste has been widely used in such developed countries as USA, France, Germany, Finland, Israel, and others. It is widely spread in rural areas where thousands of biogas power plants produce tens and hundreds millions cubic metres of biogas used for daily energy demand. In agriculture livestock manure can be used as a load for a bioreactor. The highest output of biogas is obtained from poultry litter, a slightly smaller - pig and cow manure. An average gas yield from cow manure is equal to 0.4 m^3 per 1 kilogram [16].

Microorganisms have no warmth regulations mechanisms and therefore the ambient temperature is the most important factor predetermining the rate of their reproduction and the intensity of biochemical reactions. On the basis of temperature which is the most favourable for microorganisms, they are subdivided into psychophilic, mesophilic and thermophilic. The optimum temperature for psychophilic microorganisms is 10÷20ºC, for mesophilic - 25÷37ºC and for thermophilic - 50÷60ºC [15].

The highest reproduction rate of microorganisms and intensity of their biochemical reactions are under thermophilic conditions. Alternation of a temperature regime during the process is not recommended because bacteria of one sort die and others begin to propagate.

In order to ensure anaerobic conditions the contact of the ambient air with a load inside a bioreactor needs to be avoided. Therefore, the bioreactor should be hermetic [17]. It is also necessary to maintain proper pH (the optimal pH is 7.0÷8.0) in the bioreactor and prevent incrustation on the top of the load as it impedes for the formed biogas to exit the digested raw material. The bioreactor should be equipped with the system of substrate mixing, loading and unloading. It ensures smaller variations in temperature and concentration within the load [18, 19]. Some additional quality requirements for biogas use technologies are provided in Table 3.

Table 3

Biogas use technology and quality requirements [20]

Burning in boilers	H_2S < 1000 ppm, remove moisture
Internal combustion engines	H_2S < 100 ppm, remove moisture
Microturbines	Permissible H_2S up to 70000 ppm, remove moisture
Stirling engines	Same as for boilers, only gas must be supplied at a higher pressure

Table 4

Burning heat of different sorts of fuel and organic materials [21]

Organic waste	**Dry organic matter (DOM) [%]**	**Calorific value Q_h [MJ from kg DOM]**
Green waste	95÷98	16÷19
Cattle manure	77	18÷19
Pig manure	80	18÷19
Hen manure	77	14÷16
Fuel type	**Gas production source**	**Calorific value Q_h [MJ/m^3]**
Biogas	Animal manure with or without green waste	20÷25
Natural gas	-	33÷38
Methane	-	36
Propane (gaseous)	-	93
Diesel, fuel oil, petrol	-	41÷45 MJ/kg
Liquefied propane		46
Coal	-	30÷33
Charcoal	-	14÷19

To start the fermentation process, ie the development of bacteria, the substrate can be specially prepared. However, generally, fresh manure can be used.

The technologies of biogas production from agricultural biodegradable waste are environment-friendly as they do not produce waste. In addition, all pathogens in the substrate are killed after digestion.

The calorific value of organic waste and other sorts of fuel is given in Table 4. Methane is the main and the most valuable component of biogas, while a small content of H_2 and H_2S nearly has no influence on the calorific value of biogas. If methane content is above 60%, biogas is considered to be a valuable fuel.

The aim of the work is to identify the amount of biogas evolving from pig, hen, cow manure and green waste, its composition, time required for complete digestion of the substrate, the optimal duration of substrate retention in the bioreactor.

Biogas research methodology

Investigations were carried out under laboratory conditions. In the analysis of the quantitative and qualitative content of biogas, the substrate of different composition (organic waste) was used.

For the purpose of obtaining biogas, *pig manure* (PM), *cow manure* (CM) and *hen manure* (HM) with *green waste* (GW) (grass) were used as sources for the load of the bioreactor (Table 5). These types of organic waste were selected due to the fact that their amounts generating in Lithuania are one of the biggest.

Table 5

Agricultural biodegradable waste used for investigations

Pig manure + GW [%]	**Cow manure + GW [%]**	**Hens manure + GW [%]**
99 + 1	99 + 1	99 + 1
95 + 5	95 + 5	95 + 5
90 + 10	90 + 10	90 + 10

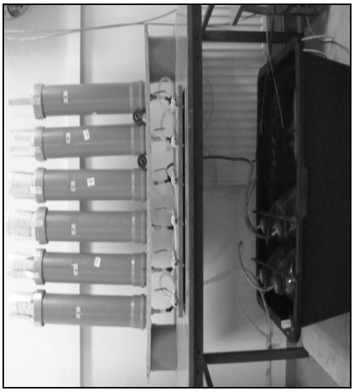

Fig. 1. A periodic operation bioreactor was used for analysis

In order to evaluate an influence of green waste on the quantity and quality of evolved biogas, 9 different substrates with different proportions of green biomass were prepared (1, 5 and 10% of the total dry mass of PM, CM and HM). Substrates were prepared for the experiment so that the total dry matters of manure and green waste made 10% of the total mass. Where a mixture contained more than 10% of the dry mass it was diluted with water. The dry part of the substrate was determined by desiccating the substrate at a temperature of 105ºC and calculated upon determining its weight before and after the desiccation.

A laboratory bioreactor of periodic operation was used for investigations (Fig. 1, Table 6). A temperature of 35 ±1ºC was maintained inside the bioreactor.

Table 6

Parameters of the laboratory bioreactor

Parameter	Bioreactor
Type of bioreactor	Laboratory bioreactor of semi-uninterrupted operation
Operating capacity [dm^3]	4.5
Mixing	Manual
Heating	Electrical
Operating temperature [ºC]	35±1

The biomass was loaded into the bioreactor of periodic operation at the beginning of the analysis and removed upon analysis completion when biogas did not evolve any longer. Biomass was not additionally supplied to the bioreactor during the experiment. The aim of this analysis was to determine the total amount of biogas evolved from the loaded biomass.

A low capacity bioreactor was used during the experiment (5 dm^3). The biomass was mixed manually once a day.

A pH analysis was performed twice: at the time of loading biomass into the bioreactor and at the end of the experiment (when the biomass was removed out of the bioreactor). Biogas was accumulated in a 4.5 dm^3 capacity tank.

The following was determined during the analysis: the amount of biogas, the concentrations of methane, hydrogen sulphide and oxygen in biogas and also pH of the digested substrate.

The value of pH was determined by a standardised potentiometric technique. Measurement was done in accordance with LST ISO 10523:1994.

The amount of biogas was measured, once a day, according to the gas volume that accumulated inside the drum.

Fig. 2. Gas analyser INCA 4000

The gas which accumulated inside the gas accumulation tank was, on a daily basis, passed through a gas analyser via a flexible hose fitted in the close end of the tank upon opening a valve. The concentration of methane, hydrogen sulphide, carbon dioxide and oxygen was measured with the analyser INCA 4000 (Fig. 2).

Device's measurement range: oxygen - 0÷25%, hydrogen sulphide - 0÷100 ppm, methane - 0÷100%.

Research results

Pig manure with green waste

Investigations covered the measurement of the quality and composition of biogas evolved during the biological digestion of pig manure (PM) mixed with green waste (GW). During the experiment's first days the amount of biogas that evolved from PM and GW was increasing and reached its highest value on the 3rd to 5th days. In the case a PM and 1% grass substrate mixture, the highest biogas yield was reached on the 5th day and it was equal to 0.697 m^3 from one cubic metre of the substrate per day (Fig. 3). Biogas evolvement lasted for 21 days. The total amount of biogas accumulated during 21 days was 6.29 m^3/m^3.

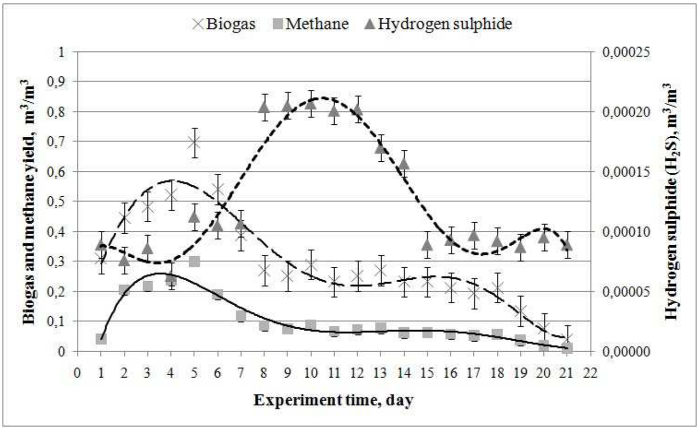

Fig. 3. Concentration of methane and hydrogen sulphide in biogas and their yield during biological digestion of pig manure with 1% of GW

On the experiment's first day the concentration of methane was 13.6%, but on the second day it jumped up to 43.3%. Afterward it was continually decreasing and at the end of the experiment reached 26.2%.

The concentration of evolving hydrogen sulphide in biogas was the highest on experiment's 7th to 14th days being as high as $204 \cdot 10^{-6}$ $m^3/m^3 \cdot d$ (207 ppm). As shown in Figure 3, at the beginning and at the end of the experiment the concentration of hydrogen sulphide was lower and used to vary between $80 \cdot 10^{-6} \div 100 \cdot 10^{-6}$ $m^3/m^3 \cdot d$.

During anaerobic digestion of PM with 5% of GW (Fig. 4), the highest amount of biogas evolved during the first 5 days of the experiment, while the largest amount of biogas accumulated on the experiment's 4th day - 0.580 $m^3/m^3 \cdot d$. The concentration of biogas that evolved from the 7th to 18th day was similar and varied from 170 to 0.230 $m^3/m^3 \cdot d$. Throughout the entire period of the experiment 5.53 m^3/m^3 of biogas evolved.

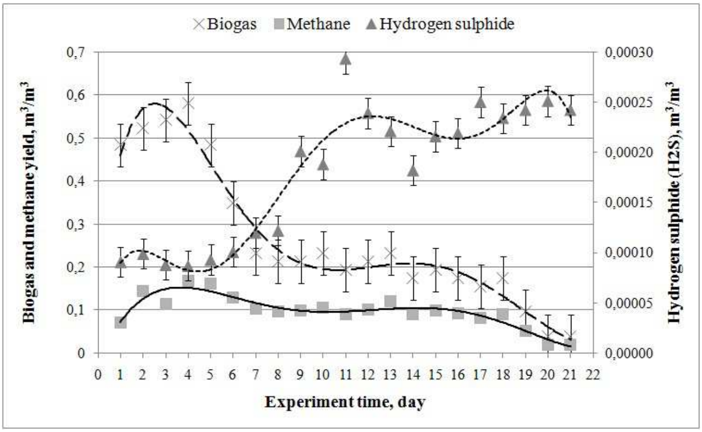

Fig. 4. Concentration of methane and hydrogen sulphide in biogas and their yield during biological digestion of pig manure with 5% of GW

On the experiment's first day the concentration of methane was 14.5% and was gradually increasing all the time. The highest concentration of methane was reached on the experiment's 13th to 21st days accounting for 53÷54%. The concentration of hydrogen sulphide was the lowest at the beginning of the experiment reaching $89 \cdot 10^{-6}$ $m^3/m^3 \cdot d$ (90 ppm). From the experiment's 6th day H_2S concentration started growing reaching its highest value on the 17th day ($246 \cdot 10^{-6}$ $m^3/m^3 \cdot d$).

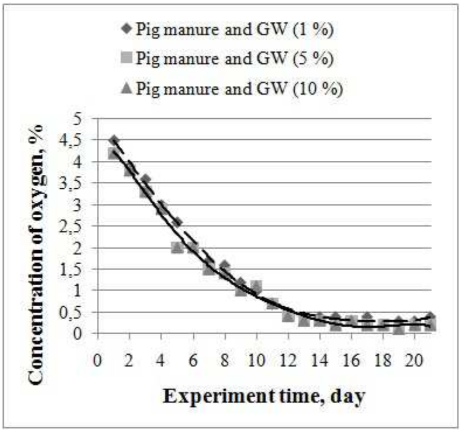

Fig. 5. Concentration of oxygen in biogas

During the experiment the concentration of oxygen (Fig. 5) was decreasing. At the beginning of the experiment the concentration of oxygen reached 4.2%, but at the end of the experiment fell to 0.2%. A decrease in the concentration of oxygen shows that anaerobic conditions were ensured. As regards the anaerobic digestion of PM with 10% of grass (Fig. 6), the highest amount of biogas evolved during the first 2 days of the experiment - 0.619 and 0.658 $m^3/m^3 \cdot d$, respectively. From the 3rd to 8th days the recorded decrease of biogas was up to 0.194 $m^3/m^3 \cdot d$. A similar amount of gas formed on the 8th to the 17th day of the experiment and varied from 0.155 to 0.213 $m^3/m^3 \cdot d$. A total of 5.57 m^3/m^3 of biogas evolved throughout the experiment.

On the experiment's first day the concentration of methane was 10.6% and was gradually decreasing all the time.

The maximal concentration of methane was recorded on the experiment's 13th - 21st days, ie 53÷54%. The concentration of hydrogen sulphide reached its highest value on the 9th - 14th days.

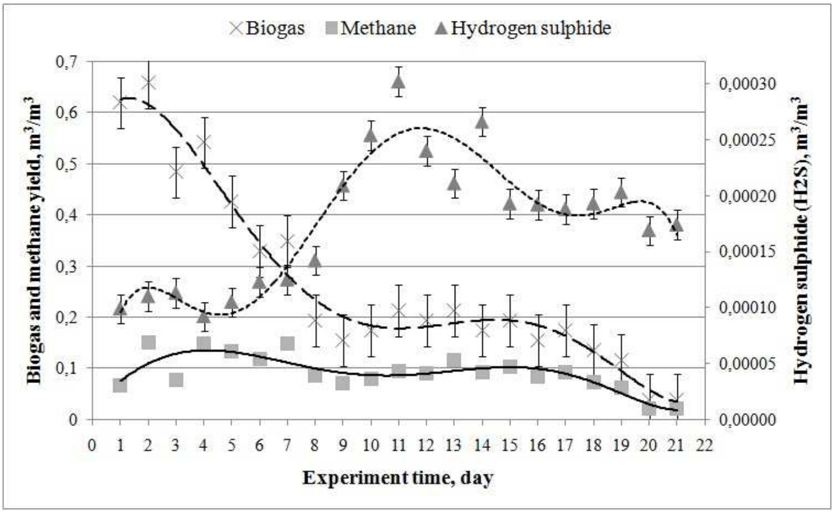

Fig. 6. Concentration of methane and hydrogen sulphide in biogas and their yield during biological digestion of pig manure with 10% of GW

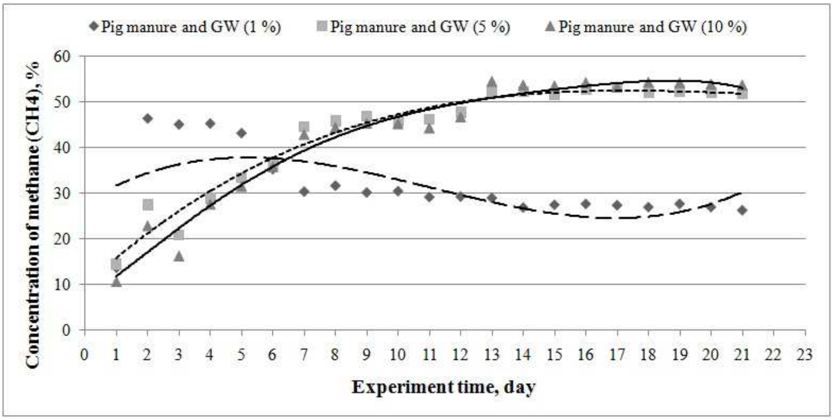

Fig. 7. Concentration of methane in different combinations of pig manure with GW

As the comparison of methane concentrations in different substrates presented in Figure 7 shows, the lowest concentration of methane throughout the experiment was in PM with 1% GW. It was influenced by a poorer C:N ratio. In the substrates which contained 5% and 10% of GW of PM dry mass, the methane concentration was higher and from the experiment's 13th day exceeded 50%.

All the substrates in question produced similar amounts of biogas. Although the highest amount of biogas evolved from PM with 1% of GW throughout the experiment, the concentration of methane was the lowest (Fig. 8).

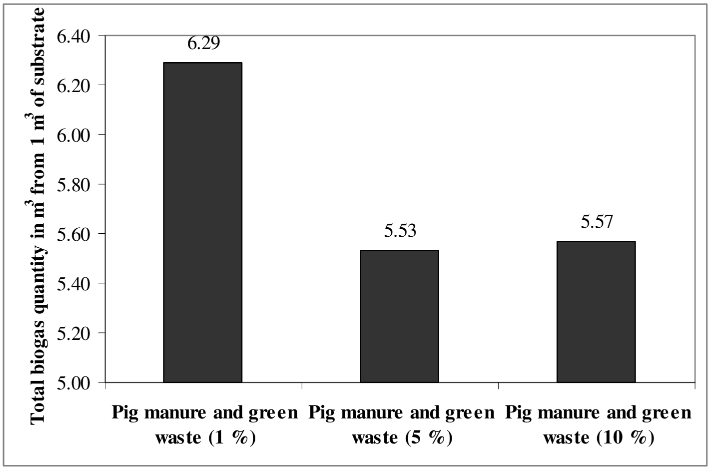

Fig. 8. Biogas amount that generated throughout the entire experiment from 1 m^3 of substrate

Hen manure with green waste

From the experiment's 1st to 3rd days a sudden increase in a quantity of biogas was observed (Fig. 9). On the experiment's second day the yield of biogas reached 0.542 m^3/m^3·d. The highest yield of biogas was recorded on the experiment's 3rd day reaching 0.813 m^3/m^3·d. After the third day of the experiment the yield of biogas began to decrease and continued decreasing until the end of the experiment. The total amount of gas produced during 14 days was 3.44 m^3/m^3.

On the experiment's first day methane concentration in the evolved biogas was minor reaching 6.2%. Afterward a growth in the concentration of methane was observed and the highest concentration was reached on the experiment's 6th day (39%). This was predetermined by an intensive process of methanogenesis. From the experiment's 7th day variations in the concentration of methane were minor and it stood at 30% at the end of experiment.

The lowest concentration of hydrogen sulphide was at the beginning of the experiment (25 ppm). Later it varied from 25 to 38 ppm.

In the beginning the concentration of oxygen reached 4.9% (Fig. 13) and was gradually falling until the end of the experiment. A reduction in the concentration of oxygen shows that anaerobic conditions have been ensured.

The pH value of the load and the substrate varied insignificantly. Load's pH was about 6.2 and the pH of the digested substrate was close to neutral, ie 6.8.

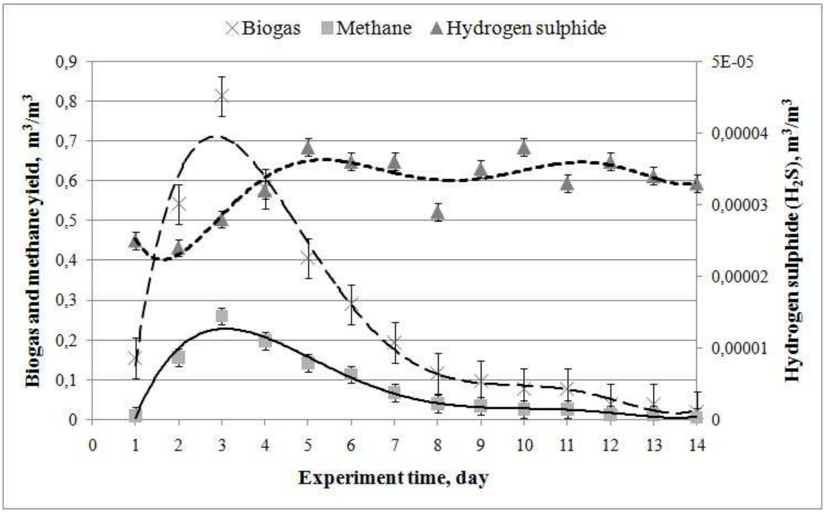

Fig. 9. Concentration of methane and hydrogen sulphide in biogas and their yield during biological digestion of hen manure with 1% of GW

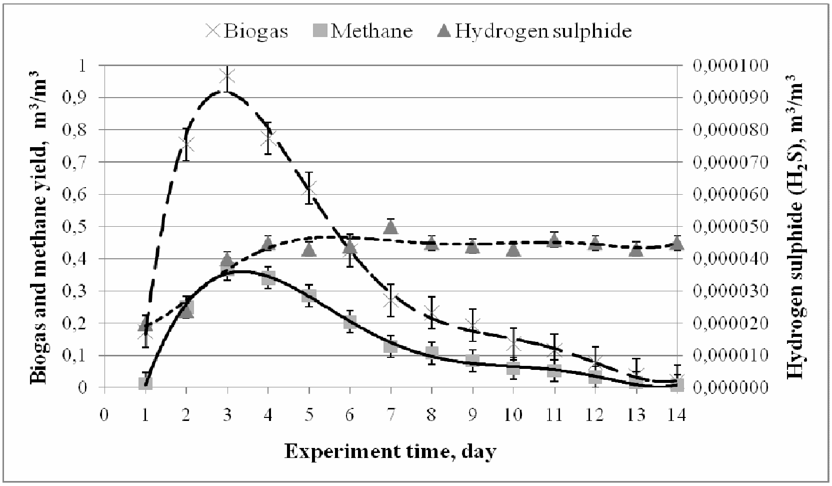

Fig. 10. Concentration of methane and hydrogen sulphide in biogas and their yield during biological digestion of HM with 5% of grass

During the anaerobic digestion of HM with 5% of GW, like in the case of 1% of GW, a significant increase in the quantity of biogas was recorded from the 1st to the 3rd day of the experiment (Fig. 10). However, the quantity of evolved biogas was higher during the first days of the experiment and the yield of biogas reached 0.754 $m^3/m^3 \cdot d$ on the experiment's second day. The highest yield of biogas, 0.968 $m^3/m^3 \cdot d$, was reached on the experiment's 3rd day. Later the amount of evolved biogas was decreasing. The total amount of biogas evolved during 14 days was 4.80 m^3/ m^3, showing a 1.36 m^3 increase against the amount of evolved biogas from the same amount of dry organic matter when using the substrate of HM with 1% of GGW (*green garden waste*).

From the beginning of the experiment the concentration of methane was increasing and on the 6th day was the highest (48%). Continuing the experiment the concentration of methane was insignificantly falling and stood at 35% at the end of the experiment. The concentration of hydrogen sulphide in biogas was the lowest at the beginning of the investigation (20 ppm). On the experiment's 4th day it rose to 40 ppm and remained similar until the end of the experiment. The concentration of oxygen (Fig. 13) at the beginning of the experiment reached 4.2% and was gradually falling until the end of the experiment. A decrease in the concentration of oxygen shows that anaerobic conditions have been ensured. The load's and substrate's pH was changing insignificantly. The load's pH was 6.1, while the digested substrate's pH was close to neutral - 6.9. When analysing a substrate mixture of hen manure and 10% of GW the maximal output of biogas was reached on the experiment's 3rd and 4th days, which was 1.060 and 1.100 $m^3/m^3 \cdot d$, respectively (Fig. 11). Further, like in the case of other mixtures of HM and GW, the output of biogas decreased. The total amount of gas evolved during 14 days was 6.33 m^3/m^3. This is the highest amount of evolved biogas out of all three mixtures of hen manure and GW. The highest value of methane concentration was measured on the 9th day (40%). However, already from the beginning of the 2nd day it reached 30% and varied from 30 to 40% until the experiment's 14th day.

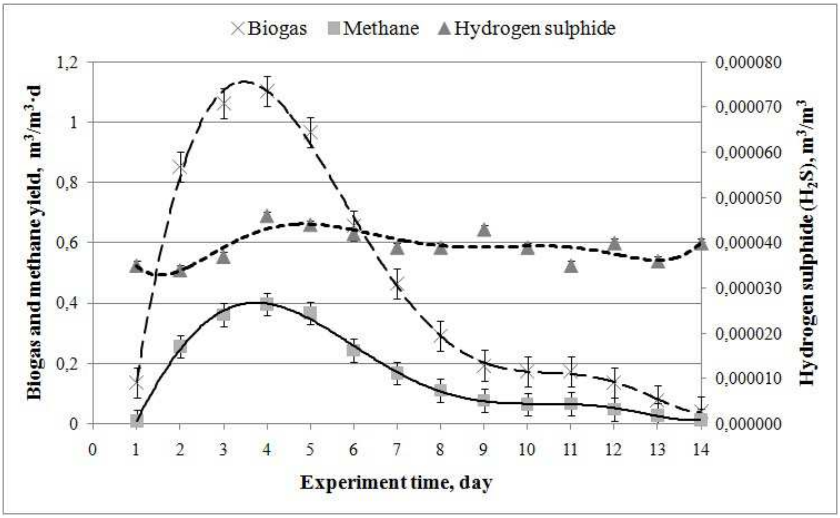

Fig. 11. Concentration of methane and hydrogen sulphide in biogas and their yield during biological digestion of hen manure with 10% of GW

The concentration of sulphur hydrogen in biogas was the lowest at the beginning of the experiment, ie (35 ppm) and varied from 34 to 45 ppm until the experiment's 14th day.

The concentration of oxygen was gradually decreasing throughout the experiment (Fig. 13). At the beginning of the experiment the concentration of oxygen reached 5.1% but at the end of the experiment it fell to 0.4%. A decrease in the concentration of oxygen shows that anaerobic conditions have been ensured.

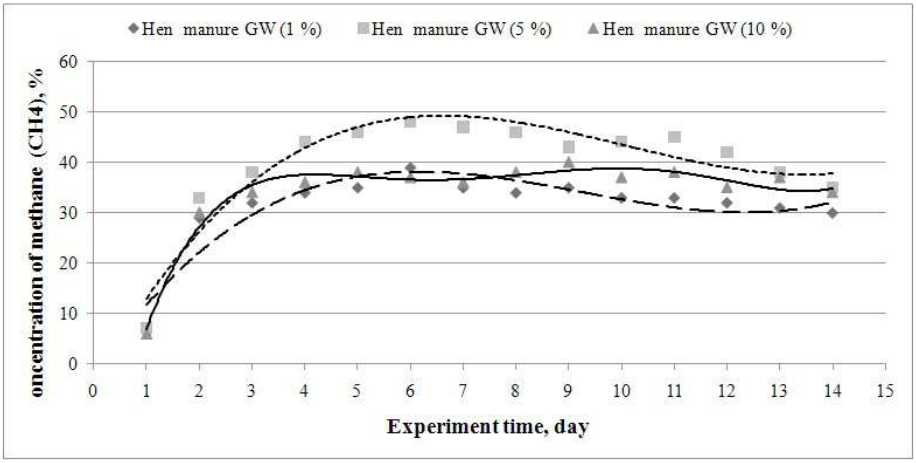

Fig. 12. Concentration of methane in different combinations of hen manure and green waste

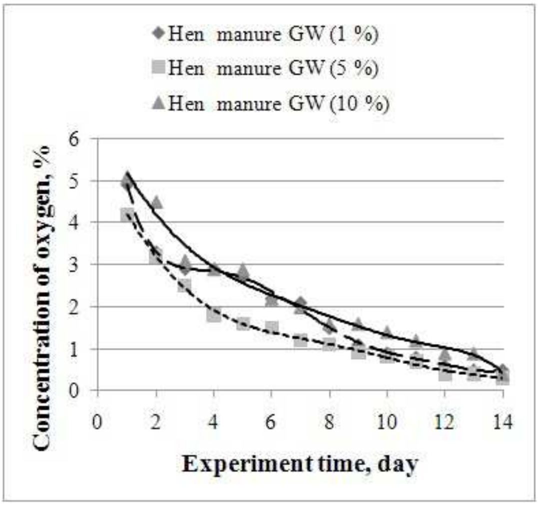

Fig. 13. Concentration of oxygen in biogas under anaerobic digestion of hen manure with GW

The pH value of the load and substrate varied insignificantly. The load's pH was about 6.2 and the digested substrate's pH was close to neutral, 6.9. This shows a well-balanced activity of anaerobic bacteria.

As the obtained results show, green waste has a positive influence on both the amount of evolved biogas and the concentration of methane in biogas.

The concentration of methane in different substrates of HM and GW was similar throughout the experiment (Fig. 12). The highest methane concentration was obtained during anaerobic digestion of HM with 5% of GW. The substrates in which grass content accounted for 5% and 10% of the dry mass of HM, methane concentration was slightly higher. This was influenced by a more favourable C:N ratio.

A comparison of the total amounts of biogas evolved during the entire experiment (Fig. 14) clearly shows the influence of GW on the yield of biogas. The highest yield of biogas was obtained with 10% of GW and the lowest - with 1% of GW.

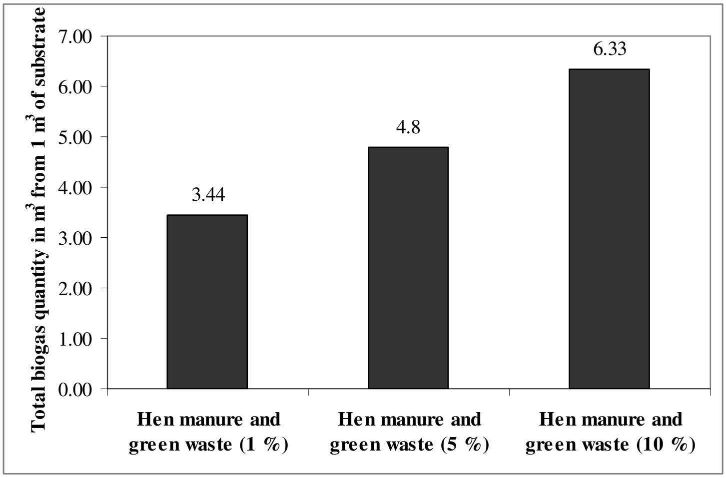

Fig. 14. The amount of biogas evolved from of 1 m^3 of substrate throughout the entire period of the experiment

Cow manure with green waste

In the process of anaerobic digestion of cow manure with 1% of GW, unlike in the case of pig and hen manure, during the experiment's first days the amount of biogas was not big (0.01 $m^3/m^3 \cdot d$). Only from the experiment's 5th day the quantity of evolved biogas began to grow and reached its maximal value on the 10th day (0.62 $m^3/m^3 \cdot d$). Further it started gradually falling. The experiment lasted for 16 days and the total quantity of evolved biogas was 4.74 m^3/ m^3.

On the experiment's 7th day the concentration of methane accounted for 42.8% and remained similar until the end of the experiment.

The concentration of hydrogen sulphide was gradually growing from 70 ppm at the beginning of the experiment and to 122 ppm at the end of the experiment (Fig. 15).

At the beginning of the experiment the concentration of oxygen was 4% (Fig. 17). Further it decreased and on the experiment's 16th hardly accounted for 0.3%. This shows that anaerobic conditions were ensured. The pH value of the load - 7.1, and upon experiment completion it changed insignificantly and remained close to neutral - 7.2. In the process of anaerobic digestion of CM with 5% of GW (Fig. 16) the highest amount of biogas evolved from the experiment's 8th to 12th days, while the largest quantity of biogas formed on the experiment's 11th day (0.619 $m^3/m^3 \cdot d$). Throughout the entire experiment a total of 5.05 m^3/m^3 of biogas evolved. On the experiment's first day the concentration of methane stood at 7.1% and was gradually increasing throughout the day. Starting from the 9th day the concentration of methane exceeded 40% and remained similar until the end of the experiment.

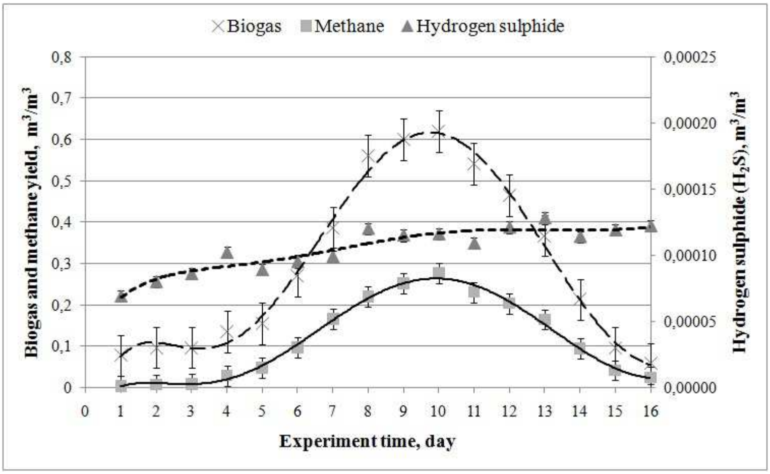

Fig. 15. Concentration of methane and hydrogen sulphide in biogas and their yield during the process of biological digestion of cow manure with 1% of GW

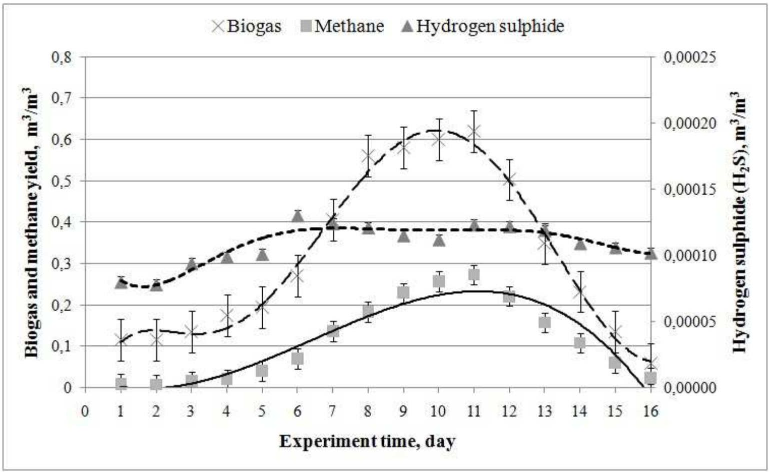

Fig. 16. Concentration of methane and hydrogen sulphide in biogas and their yield during the process of biological digestion of cow manure with 5% of GW

The concentration of hydrogen sulphide was the lowest at the beginning of the experiment reaching 78 ppm. From the 3rd day of the experiment H_2S concentration began to grow and reached its highest value on 6th day (130 ppm). The concentration of oxygen

(Fig. 17) decreased from 5.2% at the beginning of the experiment to 0.3% at the end of the experiment. Anaerobic conditions have been ensured. The load's pH was 6.9. After 16 days the digested substrate's pH remained close to neutral - 7.1.

In the process of anaerobic digestion of cow manure with 10% of GW (Fig. 18) total of 0.12 $m^3/m^3 \cdot d$ of biogas formed during the first day. From the 6th day the amount of biogas began to grow and reached the highest value (0.60 $m^3/m^3 \cdot d$) after 10 days from the beginning of the experiment. Due to the lack of nutrients for anaerobic bacteria, from the experiment's 12th day the amount of evolved biogas started decreasing. From the beginning of the experiment the concentration of methane was continually decreasing and from the experiment's 10th day exceeded 40% (Fig. 18).

The concentration of hydrogen sulphide was the lowest at the beginning of the experiment (80 ppm). Later, H_2S concentration increased and from the 5th day varied between 100÷120 ppm.

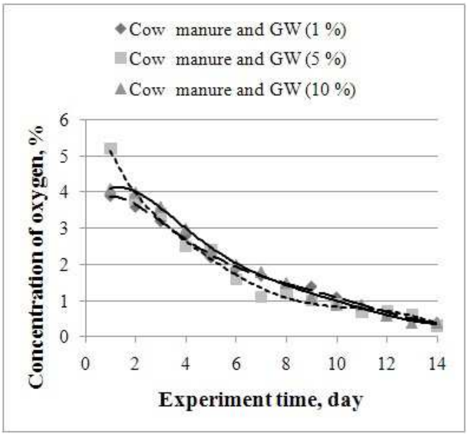

Fig. 17. Concentration of oxygen in biogas under anaerobic digestion of CM with GW

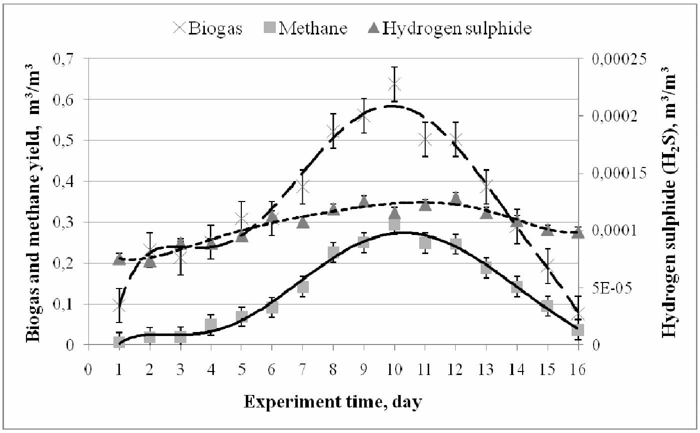

Fig. 18. Concentration of methane and hydrogen sulphide in biogas and their yield during the process of biological digestion of cow manure with 10% of GW

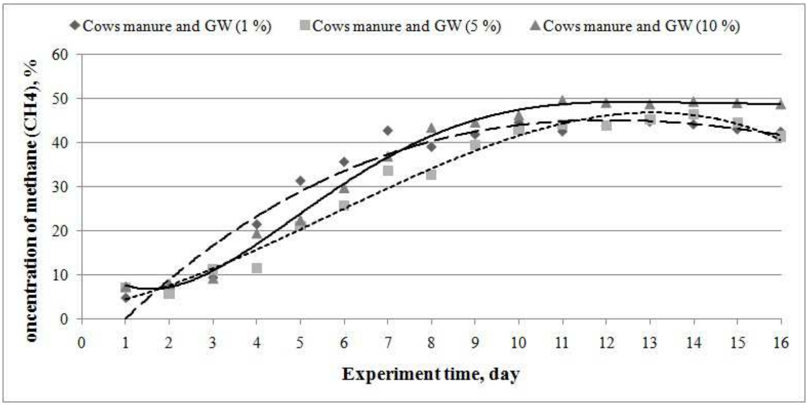

Fig. 19. Concentration of methane in different combinations of cow manure with GW

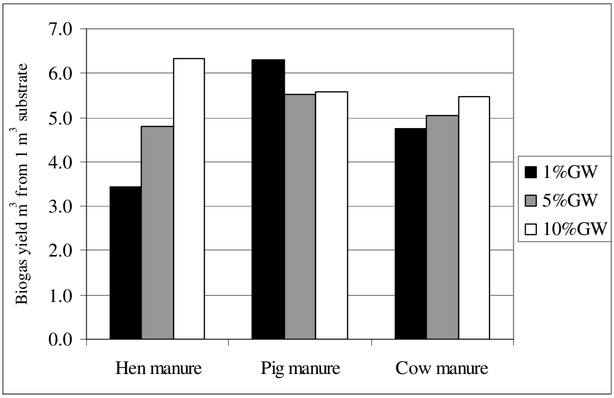

Fig. 20. The amount of biogas evolved from of 1 m^3 of substrate throughout the entire period of the experiment

The concentration of oxygen was decreasing throughout the entire period of the experiment (Fig. 17). At the beginning of the experiment oxygen concentration reached 4.1% and decreased to 0.3% at the end of the experiment. A decrease in oxygen concentration shows that anaerobic conditions have been ensured. The load's pH was 7.1. After 16 days the digested substrate's pH remained close to neutral - 7.2. In all mixtures of CM with GW the highest concentration of methane was at the end of the experiment (Fig. 19). The highest concentration of methane was achieved during the anaerobic digestion of cow manure with 10% of GW. Throughout the entire experiment the highest quantity of biogas evolved from cow manure with 10% of GW of the total dry mass of cow manure (Fig. 20).

Conclusions

1. The analysed substrates of manure and green waste can be used for the production of biogas. As the investigations show, it is appropriate to mix animal and poultry manure

with waste of vegetable origin, thus increasing the concentration of methane in biogas as well as its yield.

2. The highest quantity of biogas evolved during biological digestion of hen manure with 10% of GW. During 14 days the total quantity of evolved biogas amounted to 6.33 m^3/m^3.
3. When digesting the substrates of hen manure the highest quantity of methane concentration, 48%, was achieved with 5% of GW.
4. The highest energy value (the largest quantity of methane) was in the substrates of pig manure with GW. The concentration of methane in PM with 10% of GW reached 54.4%. Such biogas is considered to be a valuable fuel.
5. In the process of digesting cow manure with green garden waste the quantity of evolving biogas increased when the portion of GW in the substrate was increased. The total biogas quantity obtained when using cow manure with 10% of GW amounted to 5.48 m^3/m^3.
6. The concentration of hydrogen sulphide in the substrates analysed was 20÷300 ppm. Such concentration of hydrogen sulphide is not big and its usage in boilers without additional cleaning of biofuel from hydrogen sulphide is possible.
7. The amount of oxygen in evolved gas showed a decreasing tendency, and at the same time anaerobic conditions were maintained.

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BADANIA I OCENA SKŁADU CHEMICZNEGO BIOGAZU Z ODPADÓW ROLNICZYCH PODCZAS FERMENTACJI MEZOFILNEJ W WARUNKACH BEZTLENOWYCH

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Abstrakt: Fermentacja beztlenowa w reaktorach jest jedną z metod wykorzystania odpadów rolniczych na terenie Litwy. Zagospodarowując odpady w taki sposób, można uzyskać biogaz, który jest alternatywą do innych źródeł energii oraz obecnie może zastąpić gaz ziemny. W artykule zaprezentowano sposoby wykorzystania odpadów rolniczych, ulegających biodegradacji, do produkcji biogazu w komorach fermentacyjnych. W badaniach były analizowane odpady trzody chlewnej (PM), drobiu (PL) oraz krów (CD), które podlegały fermentacji beztlenowej wraz z odpadami zielonymi (GW). Udział odpadów zielonych w całkowitej masie sięgał 1, 2 lub 5% suchej masy. Odpady zielone były wykorzystane do uzyskania odpowiedniej proporcji azotu i węgla w biomasie (optymalna wartość C:N jest 25: 1), ponieważ od tych składników najbardziej zależy ilość i jakość wytwarzanego biogazu. Przed eksperymentem substrat z biomasy został zmieszany z wodą tak, że część masy suchej wynosiła ok. 10%. Badania przeprowadzono w warunkach fermentacji mezofilnej (t = 35 ±1°C). W czasie eksperymentu w biogazie oznaczono stężenie metanu, tlenu oraz siarkowodoru.

Słowa kluczowe: odpady z rolnictwa ulegające biodegradacji, fermentacja, biogaz, bioreaktor, metan

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Irena ICKIEWICZ[1]

ECOLOGICAL AND ECONOMIC ASPECTS OF MODERNIZING DISTRICT HEATING SYSTEMS IN NORTH-EASTERN POLAND

EKOLOGICZNO-EKONOMICZNE ASPEKTY MODERNIZACJI SYSTEMÓW CIEPŁOWNICZYCH W PÓŁNOCNO-WSCHODNIM REJONIE POLSKI

Abstract: On the basis of audit surveys concerning modernization of heating systems in middle-sized towns (of 16 to 65 thousand inhabitants), a technical-economic analysis as well as an ecological analysis of feasible investment projects were performed. The audit surveys concentrated mainly on 152 local low-temperature boiler houses with low emission sources in selected towns of the north-eastern Poland. The audit surveys mentioned above involved also measurements of the amounts of SO_2 and particulate matter polluting the air. The fundamental purpose of the suggested modernization of the researched heating systems was to improve the very low operating efficiency of the boiler houses (mainly with low emission sources) under concern, as well as - or perhaps above all - to reduce levels of SO_2 and particulate matter polluting the air. One of the criteria applied in the economic assessment of the suggested projects (investments) was the Net Present Value (NPV), whereas in the case of the ecological assessment - reducing air pollution.

Keywords: heat management, pollution reduction, economic effectiveness

Introduction

Air pollution with sulphur dioxide, particulate matter, and other substances, eg CO and NO_2, is regarded as the so-called primary pollution which is generated mainly during combustion of fuels in the process of energy production. The major sources of primary pollution emission are, above all, emission sources of utility and industrial power plants (the so-called high emission), and also the municipal and residential sector: local boiler houses, service companies, and individual households (the so-called low emission) [1, 2].

In order to prevent emission of global pollutants, an international agreement, called the Kyoto Protocol, was signed in 1997. The countries which ratified the agreement committed themselves to a reduction of their emissions by at least 5% from the 1990 level by 2012.

Also reducing the negative influence of humans on the natural environment (including the air pollution) is one of the European Union's priorities, and therefore, for the last several years requirements pertaining to, among others, the acceptable level of polluting the air with

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substances produced during combustion of fuels in the process of energy production, have been made more stringent.

In Poland (similarly to other EU countries), starting from 2010, the admissible level for carbon monoxide is 10 000 μg/8 h, for sulphur dioxide (SO_2) - 350 μg/m^3/h, and the concentration of the biggest particles of PM10 particulate matter (PM10 - particles whose diameter is 10 μm) amounts to 40 μg/m^3 (as the averaged value in a calendar year). In areas where pollution is very strong (eg the Silesian urban agglomeration), the term for meeting these requirements was prolonged by 3 years [3].

Sulphur dioxide comes mainly from sulphur compounds contained in combusted fuels. The concentration of sulphur dioxide in the air in Poland has been considerably reduced when compared with that in 1994, but unfortunately, since 2001 no significant reduction of the indicator of air pollution with SO_2 has been observed, similarly to the cases of reducing the levels of suspended particulate matter (PM10) and carbon monoxide (CO) (Fig. 4) [1, 4, 5].

Housing estates supplied with heat power by furnace heating are most exposed to high PM10 concentrations from primary emission resulting from fuel combustion.

Data from 2004, contained in a European Environment Agency report, indicate that the highest concentration levels of PM10 suspended particulate matter in urban areas can be found in Poland, Romania, Bulgaria, Italy, and in the Benelux countries [1, 6].

In Poland, emission of pollutants to the atmosphere is regulated by the legal provisions in force which require;

- obtaining the needed emission licences,
- obtaining allowances for emission of an adequate amount of CO_2,
- observing the so-called emission standards (for SO_2, NO_x, and particulate matter).

In order to effectively reduce the amount of particulate matter and gases in the air, produced as a result of burning fossil fuels (mainly coal), the amount of combusted coal has to be reduced, and systems for desulphurisation of combustion gases as well as dust removal devices have to be used in the first place. A basic condition of reducing fossil fuels combustion is decreasing (restricting) energy production for the purposes of central heating and hot utility water through: **thorough modernization of heating systems**, which would mainly improve their efficiency, thermomodernization of buildings, and increasing the share of renewable energy sources, such as: biomass, solar energy, wind energy, and hydropower, in energy production [2, 6, 7].

In the 1990s, the author of the present article took part in carrying out several surveys concerning energy-saving modernisation of heating systems in several middle-sized towns located in the north-east of Poland [8, 9]. These surveys aimed at reducing heat demand for the purposes connected with buildings, and thus at reducing the amount of air pollutants generated during fuel combustion. The surveys included detailed characteristics and assessment of the technical condition of the elements of the existing heating systems, ie: heat sources, heat networks and distribution centres, buildings, and their internal systems. On the basis of analysing the observed technical condition of the studied heating systems, guidelines concerning investments rationalising heat consumption by recipients were made, and economic and ‘ecological’ analyses of these investments were developed. The economic analysis pertained to modernising the existing heating systems. The NPV (*Net Present Value*) indicator as well as the *Internal Rate of Return* (IRR) were adopted as the criteria of the effectiveness of investments connected with modernising the heating systems

[10-12]. The basic criterion in the 'ecological' analysis was the reduction in the levels of PM10 particulate matter and gases polluting the air (among others, SO_2 sulphur dioxide and CO carbon monoxide), obtained as a result of modernising the heating systems [6].

Characteristics of elements of the existing heating systems in selected towns

In the second half of the 1990s, heat management in all the towns under analysis, **similarly to the situation all over Poland**, was characterised by a low thermal efficiency and it was highly damaging for the environment [1, 6, 8, 9, 13-15]. Operating efficiencies of most boiler houses, mainly these with low emission sources, were low, and they often amounted to, in the case of *central heating* (c.h.), less than 70%, and, in the case of *hot utility water* (h.u.w.) < 65%. Figure 1 presents changes of the efficiency of heating systems within the last 90 years in Poland.

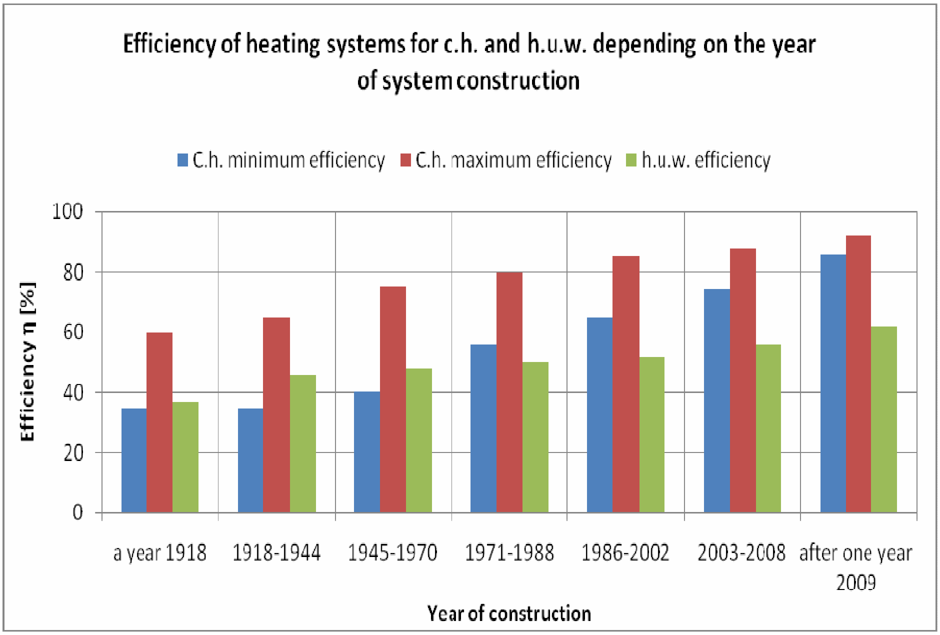


Fig. 1. Energy efficiency of heating systems for central heating (minimum and maximum) and for hot utility water depending on the year of construction [15]

In the towns under analysis, 80% of the heat distribution centres under research were energy-consuming hydrophobic centres without any automatic regulation devices. The analysed low-temperature boiler houses were equipped with boilers of the Eca IV, Rumia, etc. types which required high quality coal. The vast majority of these boilers had been used for > 15 years at that time, and therefore their technical condition was rated as unsatisfactory.

Because of their simple construction and because of being easy to operate, stoker-fired boilers were widely used for burning coal, as sources of heat and process steam both in heat engineering and in industrial plants. The main disadvantages of devices of this type were their low efficiency (the η annual average efficiency was often < 65%) and their relatively high emission of toxic gases (SO_2, CO, CO_2, NO_2). The efficiency of a properly constructed stoker-fired boiler can reach values which are a little lower than these of a pulverised-fuel boiler. The major reason for a low efficiency of a boiler (especially in heat engineering) is inappropriate selection of working parameters of the boiler, depending on the required productivity, where changes in the weather conditions force frequent changes in the boiler productivity in the wide range of the rated power [16, 17]. In the 1990s, an ‘optimal’ performance of stoker-fired boilers was ‘set’ on the basis of indirect indications such as eg combustion gas analysis. The present advancement of control engineering makes it possible to directly optimise efficiency of such stoker-fired boilers, which significantly improves efficiency of heating systems. The payback period on investments into boiler automation and metering is often much shorter than 1 year. Efficiency of heating systems after modernization (as a result of introducing automation) was increased by 12÷15% (from 62 to 75÷77%) [16-19].

Table 1

Data concerning boiler houses and heat distribution centres in the different towns

No.	Town	Heat demand	Boiler houses			Buildings equipped with		Notes
	Average perfor-mance of boilers		low-tempera-ture	high-temperature		thermo valves [%]	h.u.w. water meters [%]	
		[MW]	items	items	Heat distribution centres [items]			
1.	Suwalki 75÷81%	151.2	121	2	354, in 62% of which central heating and h.u.w. were automatically controlled	60	85	Monitoring of the system operation data
2.	Lomza 65÷78%	133	100	1	291, injection pumps in 16%	15	65	70 buildings were heated with furnaces, no automatic control in 60% of heat distribution centres
3.	Hajnowka 50÷65%	35	17	1	26, injection pumps in 96%	8	8	9 buildings were heated with furnaces, only 14% buildings with central heating systems had h.u.w.
4.	Gizycko 55÷70%	39.2	29	2	98, injection pumps in 22%	55	35	21 buildings were heated with furnaces
5.	Pisz 50÷62%	27.7	15	1	73, injection pumps in 74.7%	20.3	100	51 were heated with furnaces
6.	Siemiatycze 56÷58%	18.5	10	-	---	88	100	75.8% of all boiler houses are gas ones; they cover 48.7% of heat demand
7.	Kolno 40÷50%	14.54	19	--	58 injection pumps in 26%	84	91	Boilers in bad technical condition - 40÷50% of efficiency (100% for coal-fuelled)
8.	Czarna Bialostocka 45÷50%	15.34	26	1	23 (injection pumps or pumps in 82%)	7	97	45.6% residential buildings without h.u.w.

Boilers of the WR-5 type, burning fine coal, were installed in the researched high-parameter boiler houses; the technical condition of the boilers was rated as satisfactory. Suwalki was an exception among the analysed towns: the technical condition was estimated as good, and the existing district heating system was classified as one of the most modern systems in Poland. The above picture of the heating systems under research is indicative of their low (considering their technical potential) energy and economic efficiency and of the fact that they are relatively highly damaging for the natural environment [1, 8, 9, 15].

The data concerning the types and number of boiler houses for producing power for the purposes of central heating and hot utility water in the different towns are presented in Table 1.

Suggestions for modernising heating systems

Considering the technical condition of the heating systems analysed in the surveys, investments modernising heating systems were suggested for particular towns [8, 9, 20, 21]. The investments aimed at achieving the following two basic objectives:

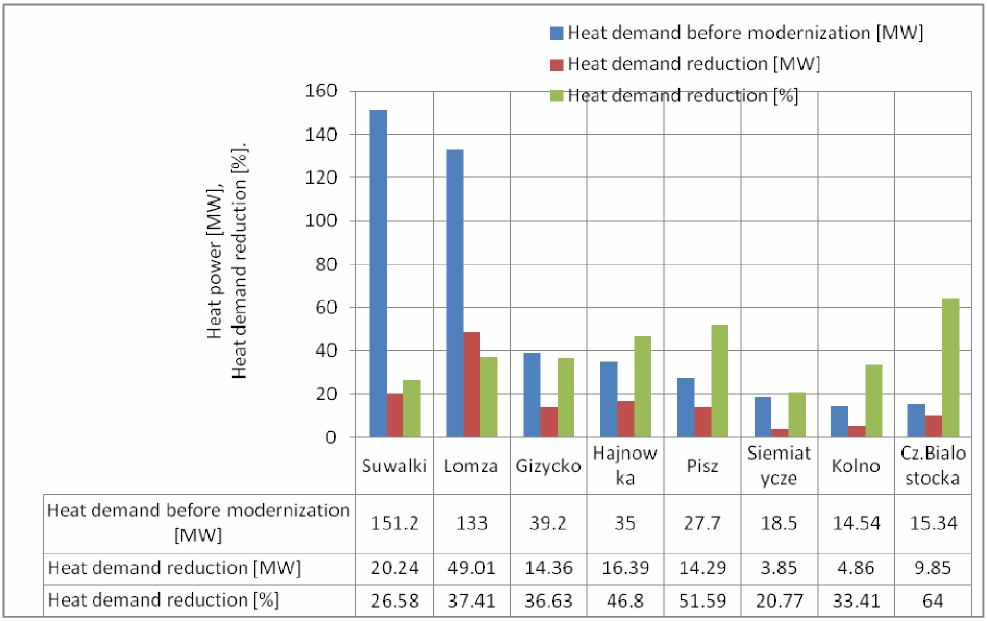
I) reducing the heat power demand through applying energy-saving technical solutions,
II) lowering the present emission of air pollutants through liquidation or modernization of the existing emission sources in the form of low-parameter coal-fuelled boiler houses and furnace heating.

Objective I is accomplished by:

- performing comprehensive thermomodernization of buildings, reducing the indicator per cubic capacity to the value of 12÷15 W/m^3, which can result in reducing the heat demand (depending on the town) by 10.78 to 24.05%, at present (in 2010) 60÷80% of this aim has been achieved (depending on the town),
- energy-saving heating of hot utility water with the use of the water from central heating systems (diminishing the maximum design heat power demand for h.u.w. purposes can reach up to 80%); the present data (from MPEC and PEC district heating companies) indicate that 40÷50% of this aim has been reached,
- using thermo valves which guarantee savings of ~20% during the whole heating period (95% of this objective has been accomplished at present),
- using h.u.w. water meters whose installation ‘forces’ users to use h.u.w., reducing consumption by ~30% (this aim has at present been reached in 100%),
- converting heat distribution centres equipped with injection pumps into automatically controlled heat exchangers, owing to which heat power consumption during a heating period can be reduced by up to 30% (this aim has at present been reached in 100%).

Effects of modernizing heat distribution centres and buildings with their internal systems (Objective I)

In order to determine the effects of modernizing heating systems (in the form of reducing heat demand), simulation calculations were performed of heat demand before and after modernizing internal systems of buildings, their thermorenovation, and modernizing heat distribution centres. The forecasted reduction in the values of heat demand for the purposes of residential buildings is presented in Table 2 and in Figure 2.



	Suwalki	Lomza	Gizycko	Hajnowka	Pisz	Siemiatycze	Kolno	Cz.Bialostocka
Heat demand before modernization [MW]	151.2	133	39.2	35	27.7	18.5	14.54	15.34
Heat demand reduction [MW]	20.24	49.01	14.36	16.39	14.29	3.85	4.86	9.85
Heat demand reduction [%]	26.58	37.41	36.63	46.8	51.59	20.77	33.41	64

Fig. 2. Reduction of heat demand in particular towns, caused by the performed thermorenovation of buildings, modernization of heat distribution centres, installing thermo valves and h.u.w. water meters, compared with the situation before modernization (before 1996)

Table 2

Forecasted reduction in the values of heat demand for the purposes of residential buildings

No.	**Town** **Number of residents**	**Reduction of heat demand for heating buildings ΔE_{co}**									**Reduction in total**	
		Heat demand	**Thermo-modernization**		**Energy-saving heating, h.u.w. water meters**		**Modernization and automation of heat distribution centres**		**Installing thermo valves**			
		[MW]	[MW]	[%]	[MW]	[%]	[MW]	[%]	[MW]	[%]	MW	[%]
1.	Suwalki 66 430	151.2	16.31	**10.78**	5.96	**3.9**	3.27*	**2.2**	14.7	**9.7**	20.24	**26.58**
2.	Lomza 63 820	133	16.20	**12.18**	16,14	**12.1**	7.9	**5.9**	8.77	**6.6**	49.01	**37.41**
3.	Gizycko 29 800	39.2	5.44	**13.88**	4.00	**10.2**	2.58	**6.58**	2.34	**5.97**	14.36	**36.63**
4.	Hajnowka 25 000	35	5.60	**16.00**	4,47	**12.8**	3.53	**10.1**	2.79	**7.9**	16.39	**46.8**
5.	Pisz 19 700	27.7	5.40	**19.49**	1.23	**4.4**	3.90	**14.1**	2.76	**9.9**	13.29	**47.89**
6.	Siemiatycze 15 060	18.5	2.64	**14.27**	0.84	**4.5**	no information	----	0.37	**2.0**	3.85	**20.77**

7.	Kolno 11 250	14.54	2.78	**19.11**	0.7	**4.8**	1.18	**8.1**	0.2	**1.4**	4.86	**33.41**
8.	Czarna Bialostocka 9700	15.34	3.69	**24.05**	1.57	**10.2**	0.96	**6.1**	2.13	**13.9**	8.35	**54.25**

[*] Suwalki - weather regulators

Having analysed the above results, it was concluded that such significant reductions of the heat power demand (20÷55%) compensate for the increased demand resulting from the prospective development of the studied towns. This produces an additional economic effect connected with eliminating capital expenditures which are necessary for possible extension of the heat sources. However, it has to be taken into account that such reduction can be obtained only if 100% of the suggested modernization works are carried out. For example, modernizing and automation of heat distribution centres should involve converting heat distribution centres equipped with injection pumps into heat exchanger distribution centres, applying energy-saving methods of heating hot utility water (h.u.w.), regulating operation parameters for central heating, regulating the h.u.w. temperature, regulating differences in the pressures of network water flowing to and out of heat distribution centres, as well as equipping heat distribution centres with heat meters.

Accomplishing objective II involves:

- modernizing (automation) of high-temperature heating systems [18, 19],
- liquidating or modernizing the existing heat sources in the form of low-parameter coal-fuelled boiler houses and furnace heating.

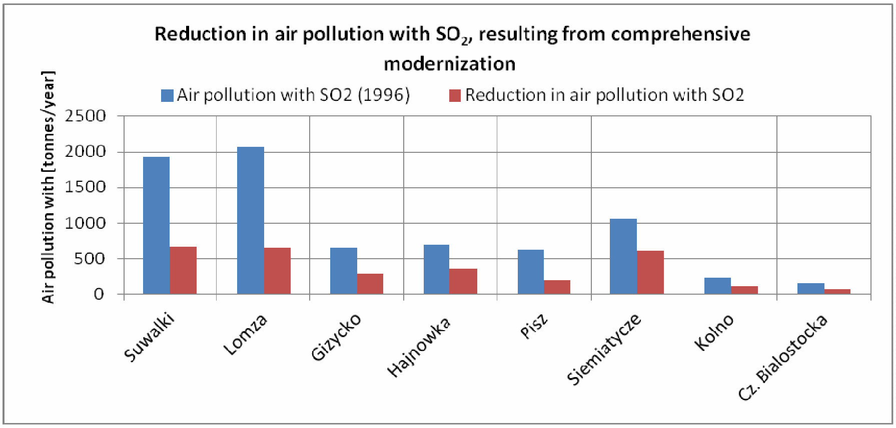


Fig. 3. Forecasted reduction in air pollution with SO_2 as a result of the performed comprehensive modernization of the heating system (accomplishment of two objectives)

Accomplishing objective II requires investing significant amounts of money because it concerns big investments such as:

- building a central heat source equipped with high-efficiency power boilers and systems of exhaust gas treatment (the source cooperates with heat distribution centres through distribution heat networks covering selected areas of towns),

- building district boiler houses equipped with high-efficiency power boilers and systems of exhaust gas treatment (the source cooperates with heat distribution centres through distribution heat networks covering selected areas of towns),
- modernizing the existing heat sources, consisting in increasing their heat power and installing systems of exhaust gas treatment (replacing the boilers used at present with high-efficiency power boilers).

Table 3

Suggested modernization of heating systems in the studied towns, and reduction in air pollution when compared with the situation in 2001

No	**Town**	**Reduction in air pollution with SO_2 to**	**Suggested modernization**
1.	Suwalki	SO_2 - 290% PM10 - 300%	Scenario I - extension of the main heating plant and the heating plant in the centre, II - extension of the main heating plant only, liquidation of the heating plant in the centre, III - extension of the main heating plant, and the heating plant in the centre is fuelled only with ecological fuel, ie natural gas or fuel oil. The remaining boiler houses should be fuelled with coal containing less sulphur. Individual boiler houses (12.8 MW) should be connected to the district heating system. Suggested scenario III.
2.	Lomza	SO_2 - 320% PM10 - 320%	Thorough modernization based on the extension of the existing system of heating plants.
3.	Gizycko	SO_2 - 230% PM10 - 250%	Gizycko - suggested scenario III - using the district boiler house and modernizing the remaining boiler houses.
4.	Hajnowka	SO_2 - 98% PM10 - 200%	Hajnowka - scenario I - building 1 central town heating plant, scenario II - 1 town boiler house supported by an industrial boiler house, scenario III - converting the selected coal-fuelled boiler houses into gas-fuelled or fuel oil ones, together with increasing the number of consumers using heat from these boiler houses. Scenario I is optimal as far as reducing pollution is concerned.
5.	Pisz	SO_2 - 318% PM10 - 300%	Liquidating coal-fuelled boiler houses, modernizing heat distribution centres. Considering great energy reserves obtained as a result of the suggested modernization, extension of the existing boiler houses is not necessary.
6.	Siemiatycze	SO_2 - 172% PM10 - 180%	Liquidating local coal-fuelled boiler houses, liquidating furnace heating, connecting to boiler houses powered by the gas network. At present (2010) there are 4 gas boiler houses and 3 coal-fuelled ones.
7.	Kolno	SO_2 - 217% PM10 - 220%	Scenario I includes constructing a Town Heating Plant (36 MW) and saving the 'old' boiler house. Both these boiler houses would have sulphur removal systems*. Liquidating smaller units in the town. Scenario II - converting 16 coal-fuelled boiler houses into 16 gas ones.
8.	Czarna Bialostocka	SO_2 - 195% PM10 - 250%	Connecting the 2 boiler houses to the heat network, savings will allow for liquidating 1 boiler in a bad technical condition. Future prospects - an exhaust gas treatment plant for the town heating plant, expanding the heat network, replacing low-parameter central heating networks with low-parameter ones.

*A highly efficient exhaust gas treatment system might lead to reducing the amounts of SO_2 and particulate matter up to 90%, and the amount of nitric oxides up to 30%.

Achieving the second (II) objective concerns big and very expensive investments. Taking this fact into consideration, 2-3 feasible scenarios were analysed and the optimum scenario (both from the financial and ecological point of view) was chosen [18]. The suggested scenarios of modernizing heating systems in the towns under research, and the resulting reduction in air pollution with SO_2 and with PM10 particulate matter are listed in Table 3 and in Figure 3.

Analysis of the economic efficiency of the investments

The required investment expenses connected with comprehensive modernization of the heating systems in the small towns under research exceeded their annual budgets, therefore a need arose for creating lines of credit with preferential treatment, making it possible to carry out the planned investments.

Assessing the economic efficiency of works connected with modernizing the heating systems under analysis was carried out with the use two types of methods:

a) methods neglecting the influence of time on the value of money; the *Simple Pay Back Time* (SPBT) and the Rate of Return are examples of such methods,

b) methods taking into consideration the value of money in time through techniques using the so-called discount. Some basic indicators applying the discount method are: the Net Present Value (NPV), and the *Internal Rate of Return* (IRR). The Net Present Value (NPV) means the difference between the values of cash flows and the investment costs discounted at a given moment in time and at the specified discount rate.

Table 4

Assessment of economic efficiency of suggested investment projects

Town	**Economic indicators for suggested scenarios of modernizing heating systems**						**Notes**
	I[*]		**II**[*]		**III**[*]		
	NPV	**IRR**	**NPV**	**IRR**	**NPV**	**IRR**	
Suwalki	+	> 100%	+	> 100%	+	> 100%	Project approved for implementation; suggested scenario III
Lomza	+	> 100%	+	> 100%	+	> 100%	Project approved for implementation
Hajnowka	-		Scenario III with the use of gas-fuelled boiler houses is acceptable				Project approved for implementation only if subsidies are granted
Gizycko	+	> 100%	+	> 100%	+	> 100%	Project approved for implementation
Pisz	+	+	Only 1 scenario was considered				Project approved for implementation
Siemiatycze	+	> 100%	+	> 100%	+	> 100%	Project approved for implementation
Kolno			No information				
Czarna Bialostocka	-		The basic and target scenarios were considered; the basic scenario was more economically beneficial				Project should not be approved for implementation because of economic reasons (economic efficiency of the investment); NPV < 0

[*] Particular scenarios are described in Table 3.

If a project is to be approved, then the NPV indicator value for this investment should be greater than zero.

The Internal Rate of Return describes the maximum interest rate for using funds, which is acceptable for the project if all the investment expenses and possible operating costs (eg paying back credit with interest) incurred during the whole period of operating are to be returned. The value of this indicator describes the discount rate for which the Net Present Value (NPV) equals zero. In other words, NPV (IRR) = 0.

If the value of the internal rate of return is higher than or equal to the adopted hurdle rate, the project can be approved [10-12]. The indicators described above were used for assessing the investment projects concerning modernization of the heating systems in the analysed towns. The results of these analyses are listed in Table 4.

After analysing the results pertaining to the economic efficiency of the suggested investments (achieving objective II), it is possible to conclude that in 5 out of the 7 studied towns all the proposed scenarios were approved for implementation (NPV > 0).

On the basis of both the performed economic and ecological analyses of the suggested scenarios, the scenarios whose implementation guaranteed better ecological effects were chosen as optimal scenarios. The suggested scenarios for different towns are listed in Table 2. Current data for particular towns under analysis show that 55÷75% of Objective II have been completed, depending on the town. It was observed that towns with a bigger number of inhabitants (Lomza, Suwalki, Gizycko) accomplished the tasks set in Objective II to a much greater extent (by 15÷25%) than the other towns (eg Czarna Bialostocka, Siemiatycze, Kolno). It results from the fact that smaller towns have smaller amounts of money at their disposal [20].

Reduction of air pollution as a result of performed modernization (data from direct measurements)

The requirements concerning air pollution with SO_2, which were in force in Poland in the period of 1997-2011, are listed in Table 5, while Tables 6 and 7, and Figures 4 and 5, show current data (as of 2010) pertaining to the air pollution with SO_2 and PM10 particulate matter for the 2 biggest towns (Suwalki and Lomza) out of the 8 towns under concern. The data for the town of Lomza concern the air pollution generated by operating the town heating plant which covers 44.5% of the heat demand.

Table 5

Acceptable levels of sulphur dioxide in the air [3]

Emission of SO_2 in Poland					
Before 1997		2005-2009		2011 (Treaty of Accession)	
[thou. Mg /year]	%	[thou. Mg /year]	reduction to [%]	[thou. Mg/year]	reduction to [%]
2 368	100	700	29.5	454	19.17

Table 6

Reduction of air pollution as a result of performed modernization

No.	**Town**	**Air pollution in [Mg/year]**				**Reduction of air pollution in comparison with 1996 [%]**			
						Forecasted*		**Present****	
		1996		2010		SO_2	Particulate matter	SO_2	Particulate matter
		SO_2	Particulate matter	SO_2	Particulate matter				
1.	Lomza	919	1180	347	71	320	320	378	602

*forecasted values (after implementing all suggested modernization procedures) - data only for the town heating plant, **continuous measurement - data from Provincial Environmental Inspection (www.wios.bialystok.pl), and MPEC Lomza

Table 7

Emission of particulate matter and gas pollutants generated by operating the town heating plant in Lomza in the period of 1996-2010 (data from MPEC Lomza)

Year	**1996**	**1997**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**
SO_2	1052	960	456	464	476	454	399	285	454	374	286	352	347
CO	176	140	34	44	38	42	39	68	67	40	39	34	42
*	440	288	106	126	114	116	108	64	66	56	54	68	71

*Particulate matter

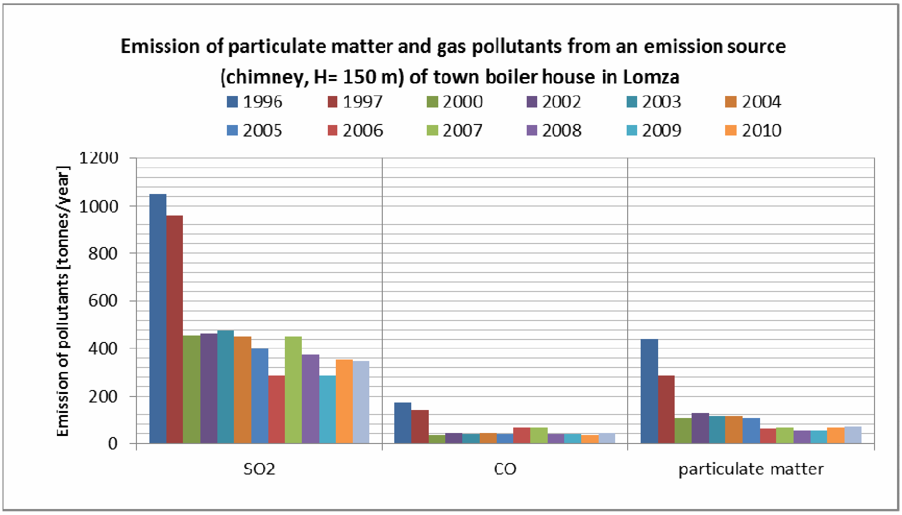


Fig. 4. Emission of air pollutants (chimney 150 m): SO_2, particulate matter, and CO in the period of 1996-2010 [www.wios.bialystok]

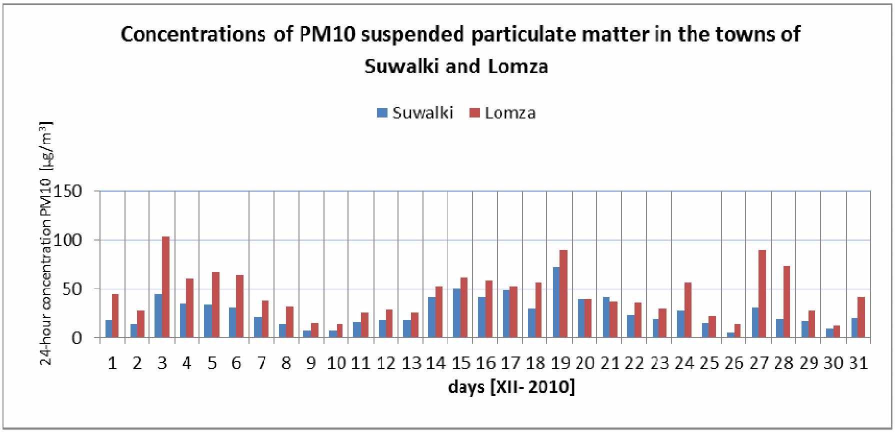


Fig. 5. Emission of pollutants with PM10 suspended particulate matter - 24-hour concentration of December 2010 - data from direct measurements in the towns of Lomza and Suwalki [www.wios.bialystok.pl]

Having analysed the emission of SO_2 on the example of the town boiler house in Lomza, it can be concluded that the performed modernization investments met the assumptions concerning the reduction in emitting SO_2, and despite subsequent rising of the relevant requirements (Table 5), the values obtained from the performed measurements do not exceed the limit values in force since 2011 (Treaty of Accession).

In the case of concentration of PM10 suspended particulate matter, the situation is worse. On the basis of the results from direct measurements (presented in Fig. 5), exceeding of limits was observed in Lomza on 13 days during only 1 month (December) out of 35 days permissible within the whole calendar year.

The situation is much better in Suwalki where the acceptable PM 10 concentration was only slightly exceeded (Fig. 5) and it took place exclusively on 1 day within this whole - winter - month.

In the remaining towns under analysis, the current situation concerning the air pollution with SO_2, CO, and PM10 is on average by 10÷20% worse than the situation in the town of Suwalki (as the biggest town out of the towns under research).

Discussion and conclusions

1. According to the Polish regulations currently in force, strategic environmental assessment is a forecast which consists in thorough evaluation of possible effects (positive or negative) resulting from implementation of projects, plans, etc. Scenario solutions are also evaluated, and the conclusions which are arrived at are used in the decision process [4, 11]. The above rules were applied to develop different scenarios of modernizing the heating systems in the analysed towns.
2. The presented results of analyses performed for 8 middle-sized towns indicate that thorough thermorenovation of buildings, modernization of internal systems (thermo valves, h.u.w. meters, etc), as well as modernization and automation of heat distribution centres can lead to saving of anything from 20 to 50% of power per one heat source (depending on the technical condition of buildings and of internal and external heating systems).
3. In the 1990s, some multi-family buildings (from 8 up to 45% - in Pisz) in all the towns under research were heated with furnaces. Moreover, a significant percentage of the analysed buildings (from 20 to 58% - in Gizycko) equipped with central heating systems did not have hot utility water (h.u.w.) systems. Considering the above, it was necessary to modernize the existing heating systems by liquidating individual heating plants in the form of low-parameter coal-fuelled boiler houses (with low emission sources), liquidating furnace heating, and by connecting some of the buildings under concern to h.u.w. systems. It often involved extending the central heating plants powered by (preferably - if there was such a possibility) gas networks, or building new heating plants.
4. Regarding the fact that investments of this kind are very expensive, the suggested solutions were analysed from the economic point of view (Table 6). On the basis of the performed economic analysis it was concluded that in 5 out of the 8 towns under concern, the NPV indicators were positive, which meant that these projects could be financially approved for implementation.

5. As a result of the performed comprehensive modernization (accomplishing objectives I and II) it was estimated that the amounts of SO_2 polluting the air can be reduced more than twofold in comparison with the amounts emitted in 2000 (depending on the town).
6. On the basis of the data obtained in direct measurements (in 2010) considering the maximum concentrations of SO_2 and particulate matter in the air for the town heating plant in Lomza, and the amounts of particulate matter for the town heating plant in Suwalki, it was observed that the performed comprehensive modernization works of the respective heating systems had produced the expected effects. In Lomza, the maximum hourly concentrations of SO_2 in the air (both the 1-hour and 24-hour concentrations) amounted to up to 50% of the acceptable values (in force since 1.01.2004), whereas in the case of PM10 suspended particulate matter, the 24-hour concentrations in Lomza were exceeded on 13 days within 1 month (out of 35 permissible days in a whole calendar year), while in Suwalki the 24-hour concentrations were in the range of 50÷100% of the acceptable values, with only one case of exceeding the limits slightly during the 31 days of the analysed winter month.
7. The values of emissions of air pollutants in the analysed 8 towns, compared with the values for other Polish towns, are not high, and they approach the permissible maximum values.The research within the last 5 years, carried out mainly by Provincial Inspectorates of Environmental Protection, shows that the registered concentration values of the basic air pollutants: SO_2 sulphur dioxide, NO_2 nitric dioxide, and suspended particulate matter in most regions of Poland, are also at satisfactory levels [1, 15]. Unfortunately, implementation of the requirements of the so-called ‘Energy and Climate Package’, including the so-called EU-ETS Directive regulating trading allowances to emit greenhouse gases (published in the EU Official Journal L 140 of 05.06.2009), to the Polish law, changes the principles of allocation of allowances for emission - ultimately, allocation of free allowances will be liquidated, and particular systems will have to receive allowances by auctioning. For heating systems (producing district heating), the Directive sets a transitional period. During this period, systems can obtain free allowances: maximum 80% of free allowances in 2013, maximum 30% of free allowances in 2020; 0% of free allowances in 2027 (the end of the transitional period). During the whole period mentioned above, the number of free allowances is to decrease constantly. Furthermore, the *Directive on Industrial Emissions* (IED) will drastically reduce the so-called emission standards. The new standards enter into force in 2016. For systems whose power does not exceed 200 MW (thermal power in fuel), this term can be extended **until the end of 2023**.
8. Implementation of the requirements of the EU-ETS and IED Directives will force changes in the structures of fuels to be used, and thus in the structures of sources, and it will also force construction of new sources as well as construction of combustion gas cleaning systems for boilers. Such operations require substantial investment costs which are impossible to pay without financial help from the outside or without effective logistics which would ensure fuel delivery safety [2, 7, 13, 21]. The moment the stringent standards on pollutant emissions enter into force, cases of exceeding maximum permissible emission standards for pollutants in many parts of some urban agglomerations (mainly of much industrialised ones) are going to be observed [22].
9. In order to meet further limitations and to reduce costs of buying allowances to emit greenhouse gases, one should aim at a maximum reduction of emitting basic air

pollutants generated during fuel combustion in the process of energy production - by optimising production and transmission efficiency, as well as monitoring of emissions of eg CO_2, and by using low- or zero-emission fuels [22, 23].

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EKOLOGICZNO-EKONOMICZNE ASPEKTY MODERNIZACJI SYSTEMÓW CIEPŁOWNICZYCH W PÓŁNOCNO-WSCHODNIM REJONIE POLSKI

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Abstrakt: Na podstawie opracowań dotyczących modernizacji gospodarki cieplnej w miastach średniej wielkości (od 16 do 65 tysięcy mieszkańców) przeprowadzono analizę techniczno-ekonomiczną oraz ekologiczną możliwych do zrealizowania przedsięwzięć modernizacyjnych. Opracowania audytorskie dotyczyły głównie lokalnych kotłowni niskotemperaturowych (152 kotłownie) z niskimi emitorami w wybranych miastach w północno-wschodnim rejonie Polski. W ramach ww. opracowań wykonano również pomiary zanieczyszczeń powietrza SO_2 oraz pyłami. Zasadniczym celem zaproponowanych modernizacji systemów ciepłowniczych było poprawienie bardzo niskich sprawności eksploatacyjnych kotłowni, głównie z niskimi emitorami, a także (a może przede wszystkim) obniżenie zanieczyszczeń powietrza SO_2 oraz pyłami. Jednym z kryteriów oceny ekonomicznej zaproponowanych przedsięwzięć (inwestycji) była *Aktualna Wartość Netto* (NPV), natomiast oceny ekologicznej - redukcja zanieczyszczeń powietrza.

Słowa kluczowe: gospodarka cieplna, redukcja zanieczyszczeń, efektywność ekonomiczna

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APPLICATION OF A GIS TECHNIQUE TO ODOUR EMISSION INVENTORY

ZASTOSOWANIE TECHNIKI GIS DO INWENTARYZACJI EMISJI ODORÓW

Abstract: Odour emissions from industrial facilities are a common cause of complaints of the population. In particular, food processing, including product and intermediate food products, and accompanying processes to get a proper taste, smell and appearance, adequate durability and increased bioavailability, may all be reasons of unpleasant odour emissions. These emissions may be associated with the occurrence of health risk or discomfort. Therefore, it seems reasonable that environmental protection activities should aim at protecting people against nuisance of odour emissions, and the first step it should be a comprehensive odours emission inventory including the location of industrial facilities that are a potential cause of odour nuisance. This paper presents results of a spatial analysis in a form of maps with the location of industrial facilities in three provinces: Mazovia, Silesia and Lower Silesia. Spatial statistical analysis allowed the evaluation of odour emission impact areas from the selected economic activities within the counties or municipalities.

Keywords: economic activity, odour nuisance, spatial analysis

A direct effect of odours exposure on human health has not been yet clearly established, even in the case of substances with very specific toxicity [1]. Commonly, numerous complaints of the population living in the vicinity of industrial facilities emitting annoying smells are the evidence of odour nuisance [2]. Main sources of odour emissions are municipal, agriculture and industrial plants. Among industrial sources the most important is food industry, including processing of meat and fish, fruit and vegetable processing, sugar, beer, milk and cooking oils [3]. To effectively assess the potential odour nuisance from agri-food industry in any area, it is essential to conduct an inventory of objects within the food industry.

This paper presents results of the conducted inventories of food industry process plants in three selected provinces: Mazovia, Lower Silesia and Silesia. GIS (*Geographic Information System*) tools were applied for visualization the spatial distribution of objects on the maps and to perform spatial statistical analysis.

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Tools and methodology

Geographic Information System (GIS) is a system of capturing, collecting, verifying, analyzing, transferring and sharing of spatial data. In a broad sense, it includes the methods and technical means, such as hardware and software, spatial databases, organization, resources and people interested in its operation [4].

GIS is increasingly being used in many fields of economy and science, including: land and buildings, planning, crisis management, mining, transport and logistics, meteorology and climatology, and increasingly in environmental protection [5, 6]. Development of GIS tools in environmental protection can effectively manage the environment, establish the boundaries of protected areas, monitor pollution in each of environmental components, predict the effects of natural disasters and predict the spread of contamination [7, 8]. Setting up and running a GIS requires clearly defined objectives and expected results, and a final structure of databases. The construction of spatial databases is an important element of a GIS project. The adopted structure of the database determines the possibilities for further implementation of various operations, such as spatial and geostatistical analyses. The planning stage is the most important phase in GIS management. The projects are working with GIS spatial data in nature. Therefore, they are not traditionally presented in a tabular form, but in a form of digital layers, where each object is represented by a point located in a particular location in space [9]. In practice, this means that the data, besides the attributes assigned to them, also have a specific location in space, defined by geographic coordinates, according to the adopted coordinate system. In Poland, the most widely used systems are PUWG 1992 (maps in scale 1:10,000 and smaller scales, in particular, topographic maps) and PUWG 2000 (maps on larger scales than 1:10,000, first of all basic and evidence maps). System PUWG 1992 provides the basis for creating topographic spatial databases, geographic, thematic hydrographic, sozological, agricultural and soil databases, and the digital terrain model, and orthophoto maps [10]. The data are obtained from different sources, depending on the needs and opportunities, usually buying them from eg state institutions such as GUS (*Central Statistical Office*) or WIOŚ (*Provincial Inspectorate for Environmental Protection*), purchasing a license to use the data (for a limited time, for a particular purpose) or by the execution or performance measurements [6]. Databases must be created or converted to such a format that can be read by GIS software. The next operation is data input by entering the spatial data and defining GIS coordinates. The results may be presented in a form of graphical presentation (charts or graphs) or tabular (reports, statistics). However, when presenting results, maps are the most common form of presentation [5].

Inventory of the objects in the food industry

The methodology for creation of GIS databases

According to the procedure of creating GIS databases, the most important was to define the objectives of the study. The present study has been conducted as an inventory of the object in the food industry. The main task was to show the spatial localization of the objects within the selected province in order to determine odour impact in the vicinity of the emission sources and to evaluate potential odour nuisance. There is a wide range of different types of food production systems. We have chosen a few processes, in terms of the odour nuisance, with the following codes of PKD7 (*Polish Classification of Activities*, 2007):

- 10.11.Z – processing and preserving of meat, except poultry and rabbits,
- 10.20.Z – processing and preserving of fish, crustaceans and mollucs,
- 10.32.Z – production of fruits and vegetables,
- 10.39.Z – other processing and preserving of fruits and vegetables,
- 10.41.Z – production of oils and fats,
- 10.42.Z – manufacture of margarine and edible fats,
- 10.51.Z – processing dairies and cheese,
- 10.72.Z – manufacture of rusks and biscuits, manufacture of preserved pastry goods and cakes,
- 10.81.Z – sugar production,
- 10.82.Z – production of cocoa, chocolate and confectionery,
- 10.83.Z – processing of tea and coffee,
- 10.84.Z – manufacture of spices,
- 10.91.Z – manufacture of prepared feeds for livestock,
- 11.01.Z – distilling, rectifying and blending spirits,
- 11.02.Z – wine production,
- 11.05.Z – beer production,
- 12.00.Z – manufacture of tobacco products,
- 14.20.Z – fur production.

Teleaddress data of the selected industrial plants in the province was obtained from the Central Statistical Office in Poland. Based on this data, the geographical coordinates were extracted for each plant and spatial databases were created. It should be noted that some problems with data quality have appeared at this stage. Despite annual update of statistical data, many addresses were outdated, or even some companies no longer existed. Missing data was another problem. Addresses were often incomplete, for instance without the street number. To give information on the degree of location accuracy for the individual objects, a special code was set with numbers from 1 to 7. '1' was for the objects with the complete addresses and coordinates, while '7' for the objects with unknown coordinates and therefore the coordinates of the nearest town were accepted for further analysis. Eventually, the database contained the following information: PKD7 code, name and location of the plant (province, district, post office, ZIP code, city, street number, property), number of employees in the plant, the location (latitude and longitude) and code accuracy.

ArcGIS Spatial Analysis and visualization of results

A ready database was entered into the ArcGIS program [11]. To specify the location of objects in space, the coordinates were defined in the database, and the coordinates system was declared. As base maps, outline maps of individual provinces and districts from IMAGIS applications were used. The same coordinate system was declared as for the data on industrial facilities (PUWG 1992). Shape files were created from the input points and then processing runs were performed on data. Figure 1 shows ArcGIS application window, while in Figure 2, the tabular data of attributes for one province under study is presented.

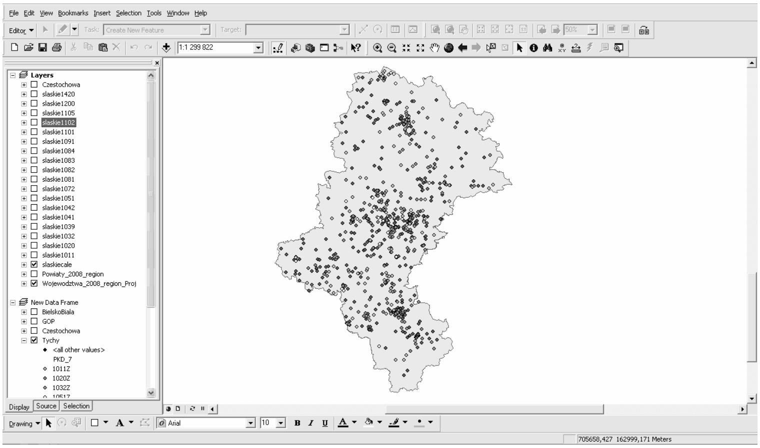
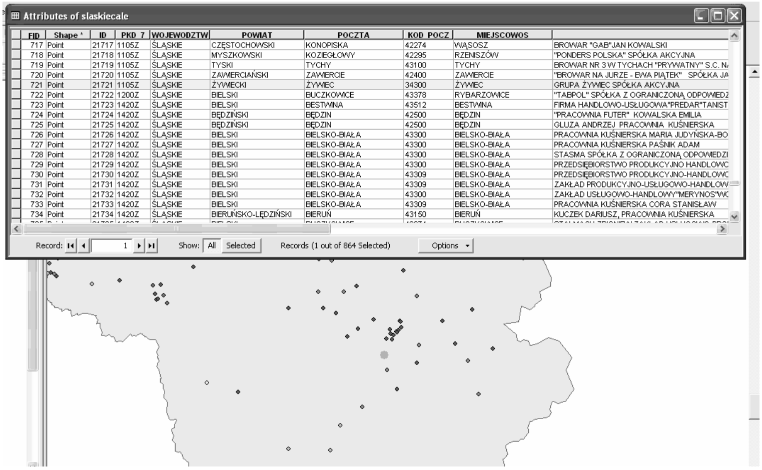


Fig. 1. ArcGIS application window


Attributes of slaskiecale

FID	Shape *	ID	PKD_7	WOJEWODZTW	POWIAT	POCZTA	KOD_POCZ	MIEJSCOWOS	
717	Point	21717	1105Z	ŚLĄSKIE	CZĘSTOCHOWSKI	KONOPISKA	42274	WĄSOSZ	BROWAR "GAB"JAN KOWALSKI
718	Point	21718	1105Z	ŚLĄSKIE	MYSZKOWSKI	KOZIEGŁOWY	42295	RZENISZÓW	"PONDERS POLSKA" SPÓŁKA AKCYJNA
719	Point	21719	1105Z	ŚLĄSKIE	TYSKI	TYCHY	43100	TYCHY	BROWAR NR 3 W TYCHACH "PRYWATNY" S.C. N
720	Point	21720	1105Z	ŚLĄSKIE	ZAWIERCIAŃSKI	ZAWIERCIE	42400	ZAWIERCIE	"BROWAR NA JURZE - EWA PIĄTEK" SPÓŁKA JA
721	Point	21721	1105Z	ŚLĄSKIE	ŻYWIECKI	ŻYWIEC	34300	ŻYWIEC	GRUPA ŻYWIEC SPÓŁKA AKCYJNA
722	Point	21722	1200Z	ŚLĄSKIE	BIELSKI	BUCZKOWICE	43378	RYBARZOWICE	"TABPOL" SPÓŁKA Z OGRANICZONĄ ODPOWIEDZ
723	Point	21723	1420Z	ŚLĄSKIE	BIELSKI	BESTWINA	43512	BESTWINA	FIRMA HANDLOWO-USŁUGOWA"PREDAR"TANIST
724	Point	21724	1420Z	ŚLĄSKIE	BĘDZIŃSKI	BĘDZIN	42500	BĘDZIN	"PRACOWNIA FUTER" KOWALSKA EMILIA
725	Point	21725	1420Z	ŚLĄSKIE	BĘDZIŃSKI	BĘDZIN	42500	BĘDZIN	GLUZA ANDRZEJ PRACOWNIA KUŚNIERSKA
726	Point	21726	1420Z	ŚLĄSKIE	BIELSKI	BIELSKO-BIAŁA	43300	BIELSKO-BIAŁA	PRACOWNIA KUŚNIERSKA MARIA JUDYŃSKA-BO
727	Point	21727	1420Z	ŚLĄSKIE	BIELSKI	BIELSKO-BIAŁA	43300	BIELSKO-BIAŁA	PRACOWNIA KUŚNIERSKA PAŚNIK ADAM
728	Point	21728	1420Z	ŚLĄSKIE	BIELSKI	BIELSKO-BIAŁA	43300	BIELSKO-BIAŁA	STASMA SPÓŁKA Z OGRANICZONĄ ODPOWIEDZI
729	Point	21729	1420Z	ŚLĄSKIE	BIELSKI	BIELSKO-BIAŁA	43300	BIELSKO-BIAŁA	PRZEDSIĘBIORSTWO PRODUKCYJNO HANDLOWC
730	Point	21730	1420Z	ŚLĄSKIE	BIELSKI	BIELSKO-BIAŁA	43309	BIELSKO-BIAŁA	PRZEDSIĘBIORSTWO PRODUKCYJNO-HANDLOWC
731	Point	21731	1420Z	ŚLĄSKIE	BIELSKI	BIELSKO-BIAŁA	43309	BIELSKO-BIAŁA	ZAKŁAD PRODUKCYJNO-USŁUGOWO-HANDLOW
732	Point	21732	1420Z	ŚLĄSKIE	BIELSKI	BIELSKO-BIAŁA	43300	BIELSKO-BIAŁA	ZAKŁAD USŁUGOWO-HANDLOWY"MERYNOS"WC
733	Point	21733	1420Z	ŚLĄSKIE	BIELSKI	BIELSKO-BIAŁA	43309	BIELSKO-BIAŁA	PRACOWNIA KUŚNIERSKA CORA STANISŁAW
734	Point	21734	1420Z	ŚLĄSKIE	BIERUŃSKO-LĘDZIŃSKI	BIERUŃ	43150	BIERUŃ	KUCZEK DARIUSZ, PRACOWNIA KUŚNIERSKA

Record: 1 Show: All Selected Records (1 out of 864 Selected) Options

Fig. 2. Tabular data of attributes for one province

The objects have been given an appropriate symbolism depending on PKD7 and the number of employees in a plant. For this purpose, classification of qualitative data was used. Differentiation of symbolism by PKD7 consisted in assigning each object, with a PKD7 code and a different color. Another data processing was to identify objects with similar PKD7 codes and to create new shape files, and then differentiation of each type of activity by the number of employees. This differentiation was based on assigning the appropriate color and size to objects according to different classes of employees: 0-9, 10-49, 50-249, 250-999, > 1000.

The results are presented graphically in a form of maps in JPG format, and in some cases, in a form of graphs. Each map is generated with basic elements such as a scale, legend and north arrow. The results are shown in Figures 3-5.

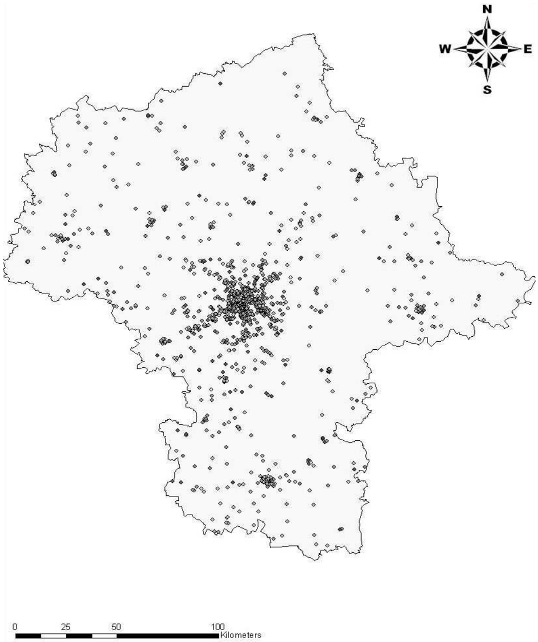


Fig. 3. Distribution of agro-food industry plants that are potential sources of odour emissions in the province of Mazovia

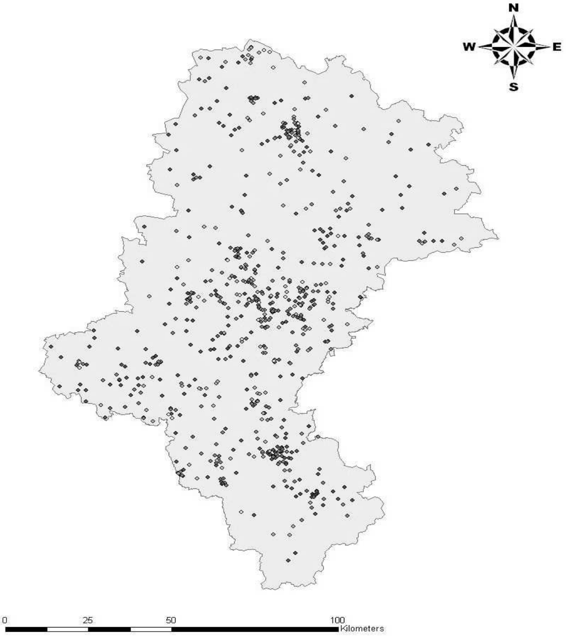


Fig. 4. Distribution of agro-food industry plants that are potential sources of odour emissions in the province of Silesia

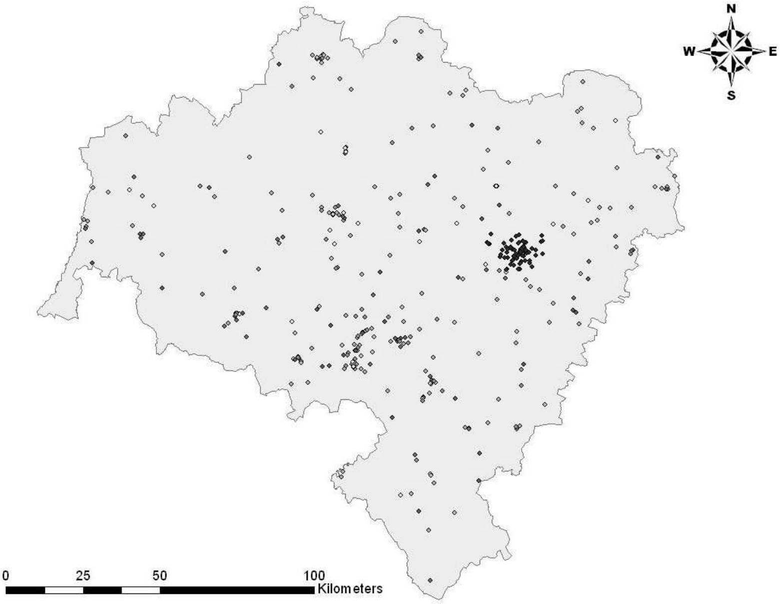


Fig. 5. Distribution of agro-food industry plants that are potential sources of odour emissions in the province of Lower Silesia

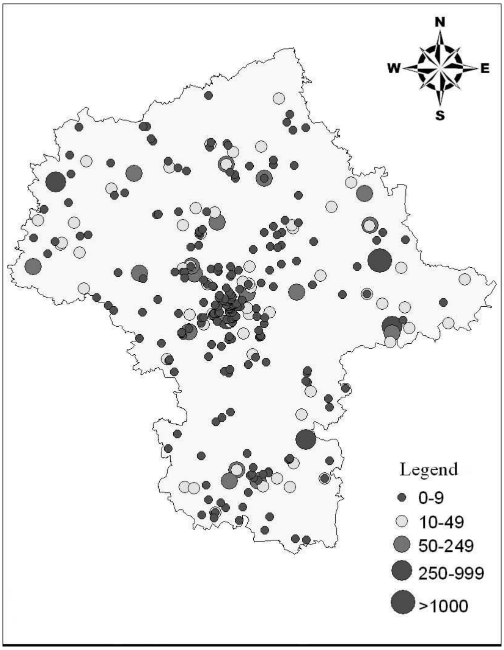


Fig. 6. Distribution of meat processing plants, except poultry and rabbits, with a breakdown of the number of employees in the province of Mazovia

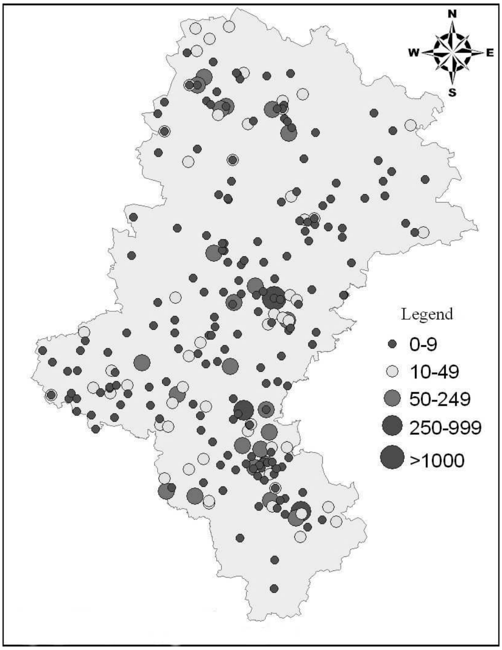


Fig. 7. Distribution of meat processing plants, except poultry and rabbits, with a breakdown of the number of employees in the province of Silesia

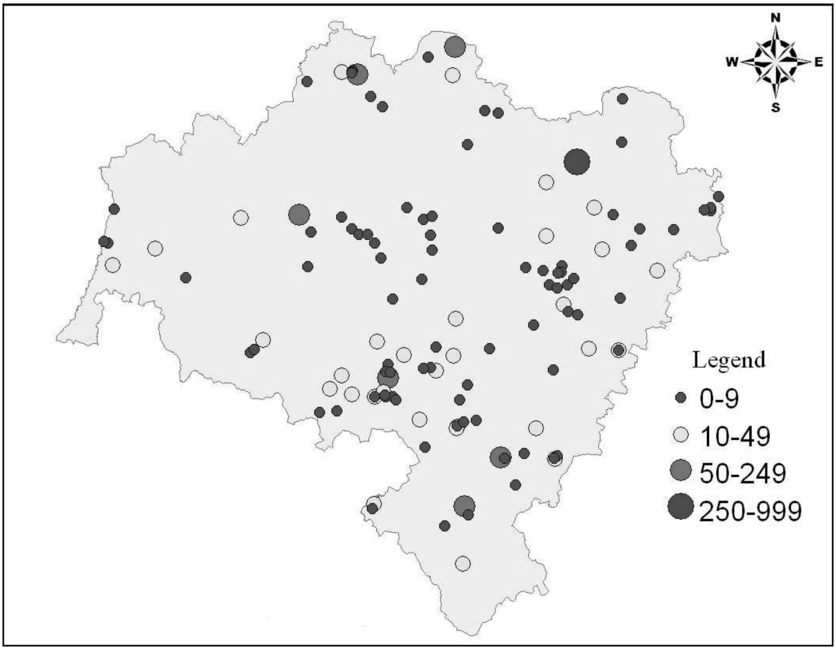


Fig. 8. Distribution of meat processing plants, except poultry and rabbits, with a breakdown of the number of employees in the province of Lower Silesia

The spatial distribution of meat processing plants, except poultry and rabbits, for three provinces are shown in Figures 6-8.

Summary and conclusions

GIS in environmental protection are becoming more widely used and play an important role especially in monitoring and environmental management. By using GIS techniques can be easily and quickly (1) located objects that are a potential source of contamination, (2) conducted observations of pollutant concentrations in all components of the environment, (3) established the boundaries of protected areas and (4) simulated the distribution of pollutants.

An inventory of odour emission sources from food processing plants in selected three provinces made it possible to determine the spatial distribution of these objects, and to quickly search for objects with certain attributes or location. The problem with high quality data acquisition was highlighted.

The probability of occurrence and the potential for odour impact were evaluated by using GIS technology. The density of industrial facilities, the type of activity, and the size and location of the plant were considered in the study. Because of the lack of information on the production amount from individual units, it was assumed that the size of the plant was proportional to the number of employees. As seen in Figures 3-5, the largest concentrations of analyzed objects are in the neighbourhood of large urban areas: in the Mazovia district around Warsaw, Silesia area GOP (*Upper Silesia Industrial District*), and around Czestochowa, Bielsko-Biala, in the Lower Silesia around Wroclaw. Based on the classification by PKD7, it can be determined which kind of activity is common in the province or the region. It was found that processing and preservation of meat, excluding poultry and rabbits (10.11.Z), processing of fruits and vegetables (10.39.Z) and fur producing plants (14.20.Z) dominate in Mazovia. In Silesia, the meat plants (10.11.Z), processing of fruits and vegetables (10.39.Z), fur production (14.20.Z), and manufacturing of rusks and biscuits (10.72.Z) are the most important industrial activities. However, in the Lower Silesia, the most common food processing plants, similar to previous cases, are meat plants (10.11.Z), fur production (14.20.Z) and plants producing biscuits (10.72.Z). In all three provinces dominate small and medium-sized companies, up to 249 employees. In the Mazovia region, 35 plants are with the number of workers over 250 (around Warsaw and Radom, Piaseczno and Ostroleka), in Silesia 12 (mostly GOP, Bielsko-Biala and around Zywiec) and in Lower Silesia region only 2 (Wroclaw and Trzebnica), respectively. Among the largest companies dominate food processing plants with codes PKD7: 10.11.Z, 10.39.Z, 10.51.Z, 10.81.Z, 11.05.Z, generally classified as odour nuisance sources. The conclusions were formulated on the basis of the analysis in ArcGIS and saved in JPG format maps.

Acknowledgement

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ZASTOSOWANIE TECHNIKI GIS DO INWENTARYZACJI EMISJI ODORÓW

Instytut Inżynierii Ochrony Środowiska, Wydział Inżynierii Środowiska, Politechnika Wrocławska

Abstrakt: Emisja odorów z zakładów przemysłowych jest częstą przyczyną skarg ludności. W szczególności przetwarzanie żywności, w tym produktów i półproduktów spożywczych oraz towarzyszących im procesów, jest przyczyną emisji zapachów złowonnych. Emisje te mogą powodować problemy zdrowotne lub dyskomfort. Dlatego wydaje się uzasadnione, aby w działaniach z zakresu ochrony środowiska, a także ochrony społeczeństwa przed skutkami emisji odorów, w pierwszej kolejności dokonać kompleksowej inwentaryzacji pod względem poziomu emisji tych zapachów oraz lokalizacji obiektów przemysłowych, będących potencjalną przyczyną zapachowej uciążliwości. W pracy przedstawiono wyniki analiz przestrzennych, w postaci map lokalizacji obiektów przemysłowych, z wybranych dziedzin działalności gospodarczych na terenie województw: mazowieckiego, dolnośląskiego oraz śląskiego. Przestrzenna analiza danych pozwoliła na określenie obszarów, na których wybrana działalność gospodarcza może być przyczyną uciążliwości zapachowej.

Słowa kluczowe: związki złowonne, działalność gospodarcza, uciążliwość zapachowa, analiza przestrzenna, GIS

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Beata GRYNKIEWICZ-BYLINA[1]

DANGEROUS PHTHALATES IN CHILDREN'S ENVIRONMENT

NIEBEZPIECZNE FTALANY W ŚRODOWISKU ŻYCIA DZIECI

Abstract: There are many chemicals in children's environment that are dangerous to their health. Some of them are eg phthalates used as plasticizers in plastic toys and in production of other articles intended for use by children. Phthalates do not form persistent connections with the polymer and migrate to the surface of the product. Children exposure to these toxic chemicals has been found to occur during licking and sucking of the product taken to the mouth by a child and during long term contact with skin. Results of tests aimed at determination of phthalates content in toys and childcare articles made in the years 2009-2011 in accredited Laboratory of Material Engineering and Environment at KOMAG according to the requirements of REACH regulation, which include limitations as regards use of the following dangerous phthalates: DEHP, DBP, BBP, DINP, DIDP and DNOP, are discussed in the paper.

Keywords: phthalates, children articles, toys, childcare articles, environment

Children are exposed to many dangerous chemical substances. Industrial activity, road transportation [1, 2], food containing preservative additives and residual pesticides [3-5] as well as consumer products made of materials containing toxic chemicals eg esters of *benzene*-1,2-*dihydrocarboxilic* acid known as phthalates [6], are the source of those chemicals. Phthalates are used in personal hygiene articles, paints, medicals and pharmaceuticals as well as in plastics used to produce floor covering, household goods, food packaging, foils and toys [7-9].

Phthalates are the plasticizers, which make polymer material eg *polyvinyl chloride* (PVC) elastic to make production of the final product easier. The following chemicals belong to phthalates: *di-2-ethyl hexyl phthalate* (DEHP), *dibutyl phthalate* (DBP), *benzylbutyl phthalate* (BBP), *diisononyl phthalate* (DINP), *diisodecyl phthalate* (DIDP) and *di-n-octyl phthalate* (DNOP) [10, 11]. DEHP and DINP phthalates are most commonly used in plastics for children due to their properties and low production costs [12-15].

Phthalates do not form covalent bonds with the polymers with which they are mixed, so they can migrate to products surface and then they can be released to the environment [16].

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Broad range of applications as well as easiness of release to the environment cause that phthalates are one of most common pollutants in rooms, where children stay. Presence of phthalates in house air and dust has been confirmed by numerous research projects [17-19].

Phthalates penetrate children organisms through digestive system and through contact with skin. Inhalation of phthalates through children respiratory system is minor source of exposure. Phthalates can be consumed together with food and swallowed dust as well as in the result of licking and sucking of objects made of plastics eg toys [20-24]. Dermal exposure is also an important way of phthalates penetration [25].

Phthalates have especially negative impact on growth and development of human fetus, infants and toddlers. They cause dysfunction of hormonal system by disturbing synthesis, concentration and action of natural hormones responsible for growth and development of sex organs, especially male genitals, and even can cause elimination of hormones [26]. Phthalates have also negative impact on children immune system causing increase of asthma and allergy cases [27].

To be cautious the European Union has introduced limitation in use of some phthalates in toys and childcare articles, including those intended for sleep facilitation, relaxation, hygiene, feeding or sucking [28]. According to the European Commission Regulation (EC) No. 1907/2006 (REACH) such phthalates like DEHP, DBP, BBP, DINP, DIDP and DNOP cannot be used in toys and childcare articles, which can be put into the mouth in a concentration higher than 0.1% in relation to the weight of the material with plasticizer. As regards other toys and childcare articles the above-mentioned limitation concerns only the following phthalates: DEHP, DBP and BBP [29].

Despite introduced restrictions, the products containing dangerous phthalates in concentration higher than accepted, intended for children, are still sold. That fact is documented in published information [30] as well as in the reports issued by Trade Inspection and by RAPEX - *Rapid Alert System for non-food dangerous products* [31, 32]. Identified cases concern exceeded content of DEHP and DINP phthalates in toys.

The published data do not provide, except a few cases, namely: soothers, feeding bottles, and cosmetics for children [33], information on the presence of dangerous phthalates in childcare articles, especially in equipment for relaxation and health, toiletries and accessories for drinking and feeding, with concentrations exceeding the limit value. Considering the fact that the above products are made of thermoplastics, including PVC, like in toys, one would expect that also in this case toxic phthalates may be present.

In the Laboratory of Material Engineering and Environment at the KOMAG Institute of Mining Technology the research project aiming at determination of phthalates contents in toys and childcare articles as well as at assessment if they meet the requirements of REACH (**R**-Registration, **E**-Evalution, **A**-Authorisation of **C**h-Chemicals) regulation was undertaken to identify the problem and to complete information in that range.

The project was realized within research task entitled: “Methodology for shaping safe environment and safe children’s life” [34]. The results of tests on toys safety, carried out in the KOMAG Laboratory within years 2009-2011, were the project merits. The results of the research project are presented in the paper.

Testing material and methodology

Determination of content of the following phthalates: DEHP, DBP, BBP, DINP, DIDP and DNOP in toys and childcare articles as well as their assessment as regards conformity with the requirements of REACH regulation were the project objective.

In total 228 of products for children were tested, including 172 toys intended for children under 36 months as well as 56 childcare articles and materials for their manufacture.

The following types of toys were tested:

- for bathing (rubber ducks and inflated toys),
- activating toys for domestic use (swings),
- to play in sand (plastic car, sand kits: bucket, shovels, rakes, molds, sandbox),
- thematic (kitchen set with plates and cups),
- on which a child can sit (rockers, vehicles),
- a child can enter (houses),
- presenting different scenes and ready models (farmyard, set vehicles),
- equipment for sports (skittles, balls),
- dolls,
- trumpets and balloons,
- simple plays and puzzles.

Childcare articles and materials for their manufacture were divided into the following groups depending on their use:

- articles for relaxation and hygiene (poufs, chairs, foils used for manufacture of mattresses in beds, strollers and for change of baby),
- articles of toilet (brushes, cups, soap dishes, containers for toothbrushes, vanity bags),
- feeding and drinking accessories (cups, cutlery, bottles, plates).

Share of each type of tested products is given in Figure 1.

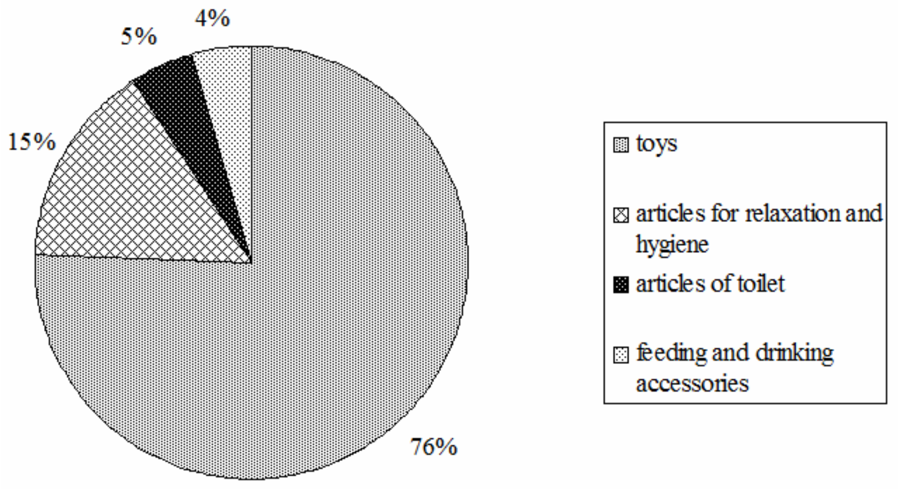

Fig. 1. Share of each type of tested products [own source]

Tested samples of products or materials used for manufacture of those products were made of different types of plastics like: *polyvinyl chloride* (PVC), *polypropylene* (PP), *polyethylene* (PE), *polyethylene of high and low density* (HDPE and LDPE), *polystyrene* (PS), *poly(acrylonitrile-co-butadiene-co-styrene)* (ABS), *poliethersulfone* (PES), *phenol-formaldehyde resin* (PF), *thermoplastic elastomer* (TPE) and rubber. Among the tested samples there were also materials, which were not identified due to lack of enough information and improper marking on the product. List of materials of tested samples of products for children are shown in Table 1.

Table 1

List of materials of tested samples of products for children [34]

Item	**Type of material**	**Number of tested products from a given type of material**			
		Toys	**Articles for relaxation and hygiene**	**Articles of toilet**	**Feeding and drinking accessories**
1.	PVC	22	20	-	-
2.	PP	23	1	5	10
3.	PE	9	-	-	-
4.	HDPE	27	-	-	-
5.	LDPE	17	-	-	-
6.	PS	2	1	5	
7.	ABS	4	-	-	-
8.	PES	1	-	-	-
9.	PF	1	-	-	-
10.	TPE	1	-	-	-
11.	PA	10	-	-	-
12.	rubber	4	-	1	-
13.	not identified	43	21	-	-

Samples of materials for determination of phthalate content were taken from toys and childcare articles or raw materials used for their manufacture by cutting out, ensuring full quantitative and qualitative compatibility of their composition to the composition of analyzed product. The taken samples were then fragmented or ground using a cryogenic mill. Two parallel samples were taken from that fragmented material and they were subjected to extraction process by the Soxhlet method. Extraction was carried out for 16 hours using dichloromethane. Two analytic samples for chromatographic analysis were taken from the obtained extract. Analytic measurements of phthalates content in the above-mentioned samples were taken on *gas chromatograph-mass spectrometer* (GC-MS). Before measurements gas chromatograph was calibrated using reference solutions of DBP, DEHP, DNOP, BBP, DIDP and DIBP phthalates. Identification of chemical compounds was made on the basis of mass spectra and retention time, and quantitative analysis was made using proper analytic algorithm. The obtained results in a form of phthalate concentration in the extract given in [$\mu g/dm^3$] were converted into phthalate mass content [mg] in the analytic sample, and then into percentage content of phthalate in relation to the material of tested product [% by weight].

General algorithm for determination of phthalate content in toys and childcare articles is shown in Figure 2.

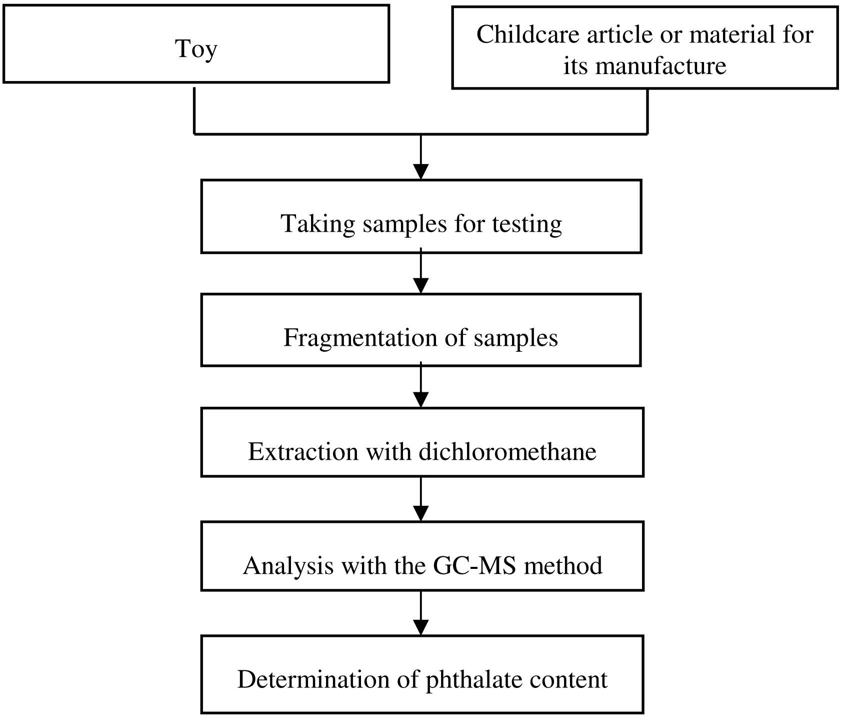

Fig. 2. Algorithm for determination of phthalate content in toys and childcare articles [own source]

Results and discussion

Analysis of determination of phthalates content in toys and childcare articles has proved presence of toxic chemical compounds in about 10% of tested samples, including: di-2-ethylhexylphthalate (DEHP), diisononylphthalate (DINP) (Fig. 3) and di-*n*-octylphthalate (DNOP).

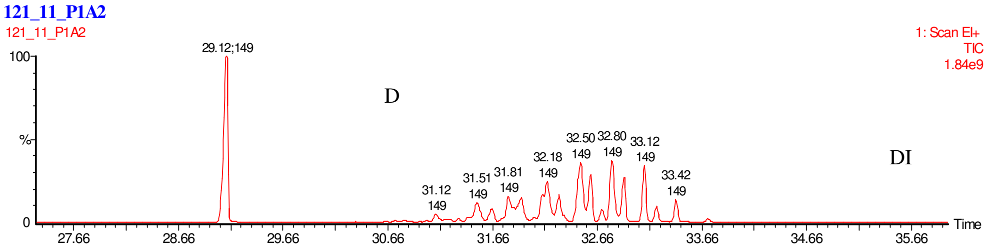

Fig. 3. GC-MS chromatogram showing the presence of DEHP and DINP phthalates in samples of PVC foil used for manufacture of mattresses for change of baby [35]

Concentration of the above-mentioned phthalates exceeded accepted value, which is 0.1%, as specified in REACH regulation. Results of analytic measurements in the rest of samples did not show phthalates presence or their concentration was below 0.05%.

Definitely greater number of exceedances of the limit content of phthalates was found in samples of childcare articles.

Shares of phthalate concentration exceedances cases in each group of tested products for children are presented in Figure 4.

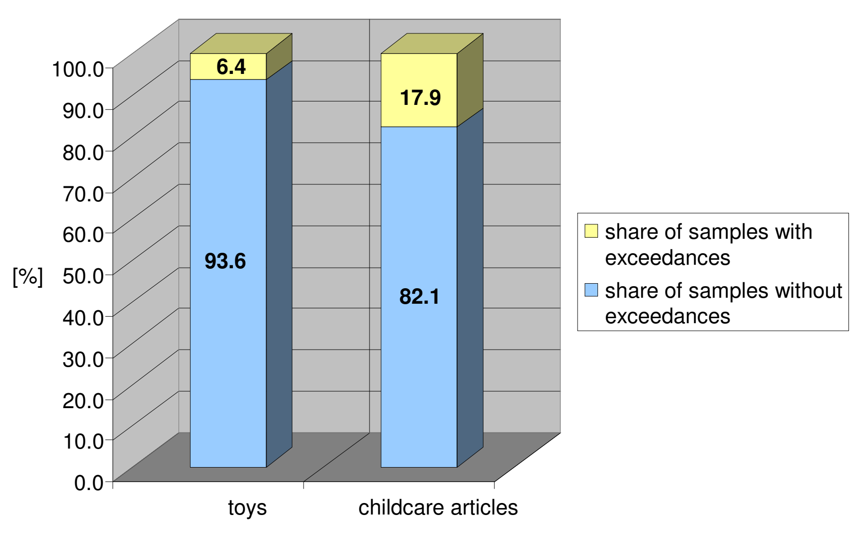

Fig. 4. Shares of exceedances of acceptable phthalate content in samples of toys and childcare articles [own source]

Polyvinyl chloride (PVC) and plastics, which were not able to be identified due to lack of any information on the product, were the materials, in which exceedances of acceptable phthalate content were reported in all tested samples.

The highest phthalate content was reported in samples of the following toys:

- inflating toys, including valves,
- toys packaging, which is a part of the toy (bag for toy carrying),
- balls,
- vehicles.

Detailed list of results of phthalates determination in toy samples, in which exceedances of acceptable values were reported are given in Table 2.

In the group of childcare articles, exceedances of permissible phthalate content were reported first of all in the samples of articles for relaxation and hygiene as well as in the samples of material used for their manufacture.

The following tested samples had the highest phthalate content:

- poufs and chairs for children,
- foils for manufacture of mattresses for children beds, strollers and for change of babies.

Detailed list of results of phthalates determination in toy samples, in which exceeding of acceptable values are given in Table 2.

Table 2

List of results from tests, which indicate exceeding of acceptable values of phthalates content in toy samples [34]

Item	Type of material	Phthalates content in toys material											
		DEHP [% by weight]		DBP [% by weight]		BBP [% by weight]		DINP [% by weight]		DIDP [% by weight]		DNOP [% by weight]	
		$x_{śr}$	u*/	$x_{śr}$	u*/	$x_{śr}$	u*/	$x_{śr}$	u*/	$x_{śr}$	u*/	$x_{śr}$	u*/
1	PVC	<0.05	-	<0.05	-	<0.05	-	**0.70**	**0.05**	<0.05	-	<0.05	-
2	PVC	<0.05	-	<0.05	-	<0.05	-	**1.08**	**0.03**	<0.05	-	<0.05	-
3	n.i. **/	<0.05	-	<0.05	-	<0.05	-	**4.13**	**0.07**	<0.05	-	<0.05	-
4	n.i. **/	**0.18**	**0.02**	<0.05	-	<0.05	-	**1.62**	**0.10**	<0.05	-	<0.05	-
5	n.i. **/	**14.63**	**0.14**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
6	n.i. **/	**0.37**	**0.12**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
7	n.i. **/	**14.8**	**0.8**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
8	n.i. **/	**12.6**	**0.8**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
9	PVC	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05		**2.02**	**0.14**
10	n.i. **/	**>20**	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
11	PVC	**0.17**	**0.02**	<0.05	-	<0.05	-	**7.67**	**0.17**	<0.05	-	<0.05	-

*/ u is extended uncertainty at confidence level 95% and extension coefficient k = 2

**/ n.i.- not identified

Table 3

List of results from tests, which indicate exceeding of acceptable values of phthalates content in materials of articles for relaxation and hygiene [34]

Item	Type of material	Phthalates content in the materials of articles for relaxation and hygiene with plasticizer											
		DEHP [% by weight]		DBP [% by weight]		BBP [% by weight]		DINP [% by weight]		DIDP [% by weight]		DNOP [% by weight]	
		$x_{śr}$	u*/	$x_{śr}$	u*/	$x_{śr}$	u*/	$x_{śr}$	u*/	$x_{śr}$	u*/	$x_{śr}$	u*/
1	PVC	**2.98**	**0.39**	<0.05	-	<0.05	-	<0.05	-	<0.05		<0.05	-
2	PVC	**5.14**	**0.68**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
3	PVC	**0.19**	**0.03**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
4	n.i. **/	**9.10**	**1.18**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
5	n.i. **/	**8.96**	**1.23**	<0.05	-	<0.05	-	**1.46**	**0.11**	<0.05	-	<0.05	-
6	PCV	**0.49**	**0.14**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
7	PCV	**0.15**	**0.02**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
8	PCV	**4.46**	**0.61**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
9	PVC	**3.52**	**0.04**	<0.05	-	<0.05	-	<0.05	-	<0.05	-	<0.05	-
10	PVC	<0.05	-	<0.05	-	<0.05	-	<0.05	**-**	<0.05	-	**1.48**	**0.2**

*/ u is extended uncertainty at confidence level 95% and extension coefficient k = 2

**/ n.i.- not identified

Conclusions

Plastics used for manufacture of toys and childcare articles contain toxic phthalates, which act as plasticizers that make structure of the material, eg PVC, elastic. Phthalates, due to their chemical properties - lack of covalent bond with the plastic, migrate to the surface of the product's material and are the source of hazard for children. Phthalates that are on the surface can be consumed by children in a result of sucking and licking as well as they can penetrate children bodies in a result of direct contact with skin.

The tests proved that some of the dangerous phthalates are still in use in products for small children not only in toys, but also in childcare articles.

The tests identified exceedances of permissible content of the following phthalates: di-2-ethylhexylphthalate (DEHP), diisononylphthalate (DINP), di-n-octylphthalate (DNOP). They were present especially in the samples of toys intended for children under 36 months, which can be taken to mouth as well as in the samples of articles for relaxation and hygiene made of PVC and the plastic, information of which was not placed on the product.

The tests carried out so far indicated for a need of further tests for the specified group of materials to verify their conformity with the requirements of REACH declaration.

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NIEBEZPIECZNE FTALANY W ŚRODOWISKU ŻYCIA DZIECI

Abstrakt: W środowisku dziecka występuje wiele niebezpiecznych dla jego zdrowia substancji chemicznych. Jednymi z nich są ftalany, stosowane jako plastyfikatory tworzyw sztucznych w produkcji zabawek i innych wyrobów przeznaczonych do stosowania przez dzieci. Ftalany nie tworzą trwałych połączeń z polimerami i migrują na powierzchnię produktu. Narażenie dzieci na ekspozycję tych toksycznych związków chemicznych występuje przede wszystkim w trakcie lizania i ssania produktu wkładanego do ust przez dziecko oraz podczas długotrwałego kontakt z jego skórą. W publikacji przedstawiono wyniki badań zawartości ftalanów w zabawkach i artykułach pielęgnacyjnych przeznaczonych dla dzieci przeprowadzone w latach 2009-2011 w akredytowanym Laboratorium Inżynierii Materiałowej i Środowiska ITG KOMAG, zgodnie z wymaganiami rozporządzenia REACH, wprowadzającego ograniczenia w stosowaniu niebezpiecznych ftalanów: DEHP, DBP, BBP, DINP, DIDP i DNOP.

Słowa kluczowe: ftalany, produkty dla dzieci, zabawki, artykuły pielęgnacyjne dla dzieci, środowisko

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Zofia MACHOWICZ-STEFANIAK[1*] and Ewa ZALEWSKA[1]

OCCURRENCE OF *Colletotrichum dematium* ON SELECTED HERBS SPECIES AND PREPARATIONS INHIBITING PATHOGEN`S GROWTH AND DEVELOPMENT *IN VITRO*

WYSTĘPOWANIE *Colletotrichum dematium* NA WYBRANYCH GATUNKACH ZIÓŁ ORAZ PREPARATY OGRANICZAJĄCE WZROST I ROZWÓJ PATOGENU *IN VITRO*

Abstract: The studies investigated the occurrence of little known in Poland fungus *Colletotrichum dematium*, found in 2005-2010 on the plants of caraway and angelica in 2008-2010, cultivated in the Lublin region. The effectiveness of some preparations in inhabiting the growth and development of the pathogenic strain K 426 *C. dematium* was studied. The effect of biotechnical preparations Biochikol 020 PC (chitosan 20 g/dm^3) and Biosept 33 SL (33% of grapefruit extract) and 11 fungicides from different chemical groups was examined. The method consisted of adding the preparation in use form to sterile culture medium and inoculation of the pathogen inoculum. The colonies of *C. dematium* growing on the medium without preparations constituted the control. The percentage of growth inhibition after 4 and 8 days of growth, the type of toxic activity, inhibition of morphological structures formation and causing degeneration of pathogens mycelium were adopted as the criteria to assess the activity of preparations. Biosept 33 SL, and fungicides Dithane Neo Tec 75 WG and Helm-Cymi 72.5 WP were recognized as the most effective in reducing the growth and development of the pathogen.

Keywords: *Colletotrichum dematium,* occurrence, Biochikol 020 PC, Biospet 33 SL, fungicides

The genera *Colletotrichum* include numerous species of fungi that occur in all climatic zones. *C. dematium* (Pers. ex Fr.) Grove is a typical species of genera. This is a saprotroph secondarily inhabiting the dead parts of plants, and pathogenic strains of this fungus can cause diseases, so called anthracnose of different species of host plants [1]. *C. dematium* was recognized as the pathogen of catharanthus - *Catharantus roseus* plants in Florida [2], spinach in Australia [3], Japanese radish in Japan [4] and strawberries in India [5]. In Poland, this fungus was isolated from the caraway (*Carum carvi*) plant in recent years and from year to year it occurred with increasing frequency [6]. In accordance with the rules of Koch, the ability of the tested strains of *C. dematium* to cause necrosis and dieback of

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seedlings sprouted caraway was shown [7]. The occurrence of this fungus in Poland on one of the rush vegetation species - *Iris pseudocyperus* was noted by Mazurkiewicz-Zapalowicz et al [8] on rhubarb rootstock by Robak [9], on decaying stems of *Calamagrostis arundinacea* by Chlebicki [10], and on spinach by Mikolajska and Majchrzak [11]. Pathogenic strains of fungi produce phytotoxic, bioactive metabolites [12].

C. dematium can also be harmful to warm-blooded organisms, including the human. It was noted that the secondary metabolites of fungus were the cause of keratitis of a farmer in India [13]. Given the increased importance *C. dematium* as a plants pathogen, the fundamental research into the possibility of limiting the growth and development of the fungus with some biotechnical and chemical preparations was carried out.

Material and methods

The occurrence of fungus

Cultures of *C. dematium* used in the study were isolated in 2005-2010 from various organs of caraway plants and in 2008-2010 from angelica (*Angelica archangelica*) plants cultivated in the Lublin region (Table 1). The isolation of fungus was conducted using artificial culture method on malt medium solidified with agar - Difco [14]. Strain K 426 of *C. dematium* obtained earlier from caraway plant cultivar Konczewicki with necrosis symptoms [6], and recognized in pathogenicity tests as the most pathogenic to this plant was chosen to the present study from our professional collection of fungi.

Table 1

Occurrence of *C. dematium* on caraway *Carum carvi* L. in 2005-2010
and on angelica *Archangelica officinalis* Hoffm. in 2008-2010

Years / Species of plant	Frequency of occurrence					
	2005	2006	2007	2008	2009	2010
Carum carvi L.	+	+	++	+	+	++
Archangelica officinalis Hoffm.				-	+	++

+ frequency of occurrence < 5%, ++ frequency of occurrence from 5 to 10%

The effect of preparations on *C. dematium*

Biotechnical biopreparates ie Biochikol 020 PC - chitosan 20 g/dm^3, Biospet 33 SL - 33% extract from seeds and pulp of grapefruit and 11 fungicides from various chemical group were used in the studies of the effect of various compounds on *C. dematium in vitro* (Table 2). All experiments were performed in two series. The method used in the studies consisted of adding the preparation used to the sterile culture medium cooled to 50°C and inoculating the studied fungus inoculum on this medium [15]. Biochikol 020 PC was tested at the following concentrations: 0.01%; 0.025%; 0.05% and 0.1%, and Biospet 33 SL in concentrations: 0.05%; 0.1%; 0.2% and 0.3%. Fungicides were tested at the concentrations of 1, 10 and 100 ppm a.i., with the aim of determining an approximate ED_{50} dose and arranging them in one of four groups of fungicidal activity according to Borecki [15]. Group I - ED_{50} less than 1 ppm - substances strongly fungicidal, Group II - ED_{50} between 1 ppm and 10 ppm - strong fungicidal substances; Group III - ED_{50} between 10 ppm and 100 ppm - substances of moderate antifungal activity; Group IV - ED_{50} above 100 ppm - substance with weak or no antifungal activity. The type of toxic activity on *C. dematium* for fungicides was also defined. In the experiment with Biochikol 020 PC poor malt medium Difco, ie reduced by half the amount of maltose per litre was used [16]. On the other hand, the studies of the effect of Biosept 33 SL and fungicides were conducted on PDA medium (Difco) [15, 17]. Mycelial disk (3 mm diameter) taken from two-week-old, one-spore colonies growing on PDA medium, at the temperature 24°C constituted the infection material. For each preparation as well as for each studied concentration of preparation and for fungi, four replications were made. The colonies of *C. dematium* growing on the medium without preparations constituted the control.

Table 2

List of examined fungicides

No.	**Fungicides**	**Name of active ingredient and its content in the fungicide**	**Producer**
1	Amistar 250 SC	250 g/dm^3 - azoxystrobin	Syngenta Limited
2	Bravo 500 SC	500 g/dm^3 - chlorothalonil	Syngenta Limited
3	Discus Top 675 WG	85 g/dm^3 - kresoxim-methyl; 590 g/dm^3 - methiram	BASF AG - Niemcy
4	Dithane Neo Tec 75 WG	75% - mancozeb	Dow Agro Science Polska Sp. z o.o.
5	Gwarant 500 SC	500 g/dm^3 - chlorotalonil	Arysta LifeSciences
6	Helm-Cymi 72.5 WP	4.5% - cymoksanil; 68% - mancozeb	Z.CH. “Organika-Sarzyna” S.A.
7	Kaptan 50 WP	50% - captan	Z.CH. “Organika-Azot” Jaworzno S.A.
8	Mildex 711.9 WG	66.7% - fosetyl aluminium; 4.4% - fenamidone	Bayer CropSciences S.A.
9	Rovral Flo 255 SC	255 g/dm^3 - iprodione	BASF Polska Sp. z o.o.
10	Tanos 500 WG	25% - cymoksanil; 25% - famoksat	Du Pont de Nemours (France) S.A.S.
11	Topsin M 500 SC	500 g/dm^3 - tiophanate methyl	Sumi-Agro Poland Sp. z o.o.

The measure of the activity of the test preparations was the percentage of growth inhibition after 4 and 8 days of cultivation of fungus colonies in the presence of preparations in relation to the control colony, according to Kowalik and Krechniak [18] formula:

$$I = \frac{C - T}{T} \cdot 100\%$$

where: I - percentage of inhibition, C - diameter of control colony [mm], T - diameter of colony growing on medium with preparation [mm] according to Kowalik and Krechniak formula [18]. The obtained data were statistically analyzed.

The microscopic observations of 4- and 8-day-old colonies of *C. dematium* were also carried out, in order to detect changes in the appearance of morphological structures of the fungus under the influence of preparations. In the absence of fungal growth on the medium containing the preparation the type of toxic activity according to Borecki was determined [15]. To this end, the fungus inocula were transferred to Petri dishes with PDA medium without preparation. After several days of cultivation of so prepared dishes at a temperature of 24°C, the type of toxic activity was determined on the basis of studies on the growth or death of the colony.

Results

The first cultures of *C. dematium* obtained from caraway plants, cultivated in the Lublin region were isolated in 2005. In subsequent years, isolations repeated, especially from plants in the second year of cultivation. In the period 2005-2010, the fungus was found on 1.2% to 10% of plants (Table 1). The fungus inhabited the aboveground plant parts, mostly leaves, shoots and umbels and roots in a smaller degree. The presence of *C. dematium* on angelica plants was observed in 2009-2010 on leaves of plants in the first years of cultivation and on shoots of plants growing in second year of cultivation. The fungus did not cause any specific symptoms of anthracnose on plants of caraway and angelica, but many cultures of them were isolated on artificial culture medium. They formed a dark gray, almost black, velvety mycelium. Some isolates tinged the substrate purple. Appessoria, acervuli with numerous setose and conidia occurred in the microscopic examination of isolates (Figs 1-4).

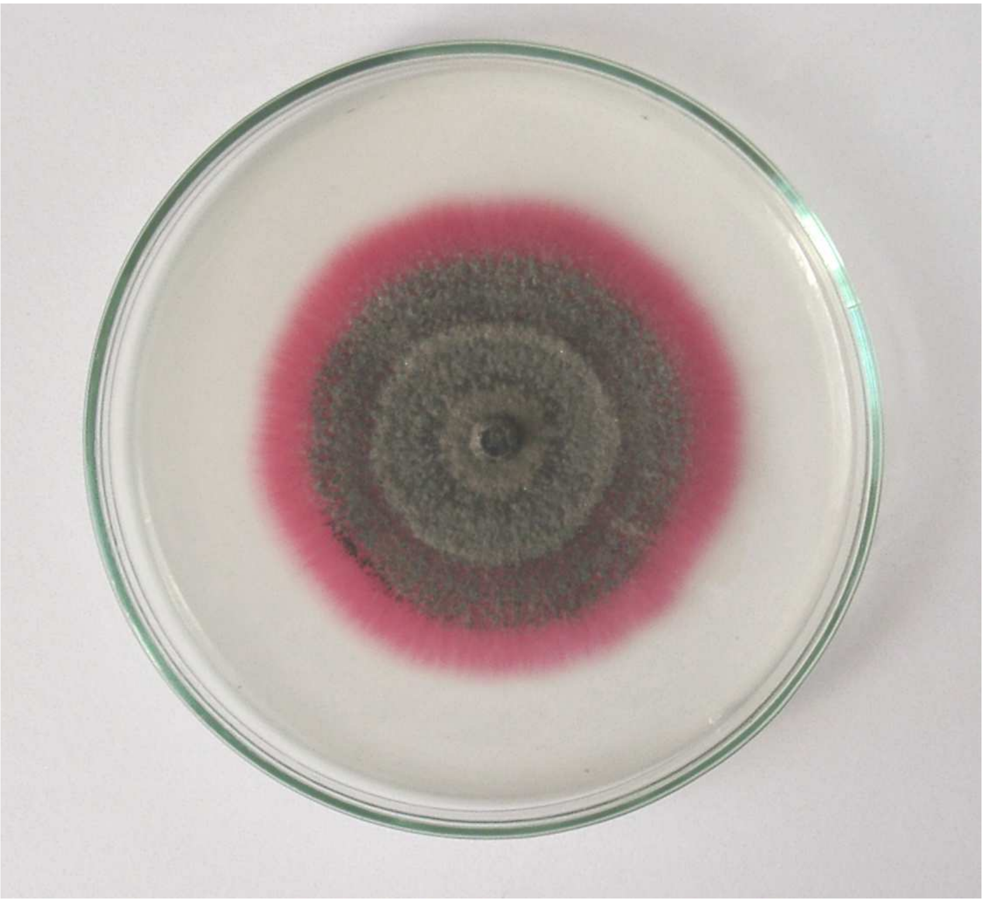

Fig. 1. 14-day-old colony of *C. dematium* isolate K 425 on the PDA medium, at 25ºC (Photo E. Zalewska)

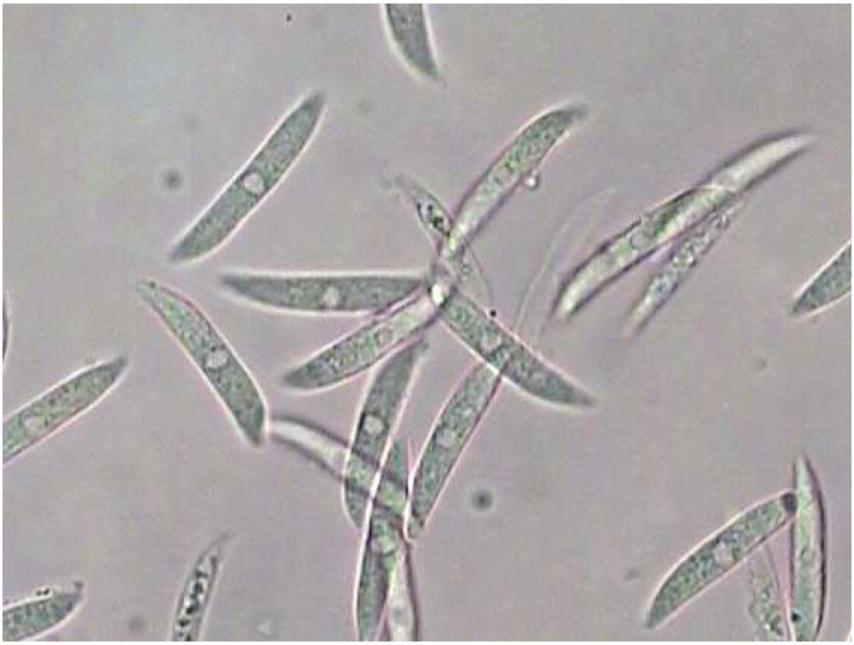

Fig. 2. Conidia of *C. dematium* in light photo microscope, magnification x750 (Photo E. Zalewska)

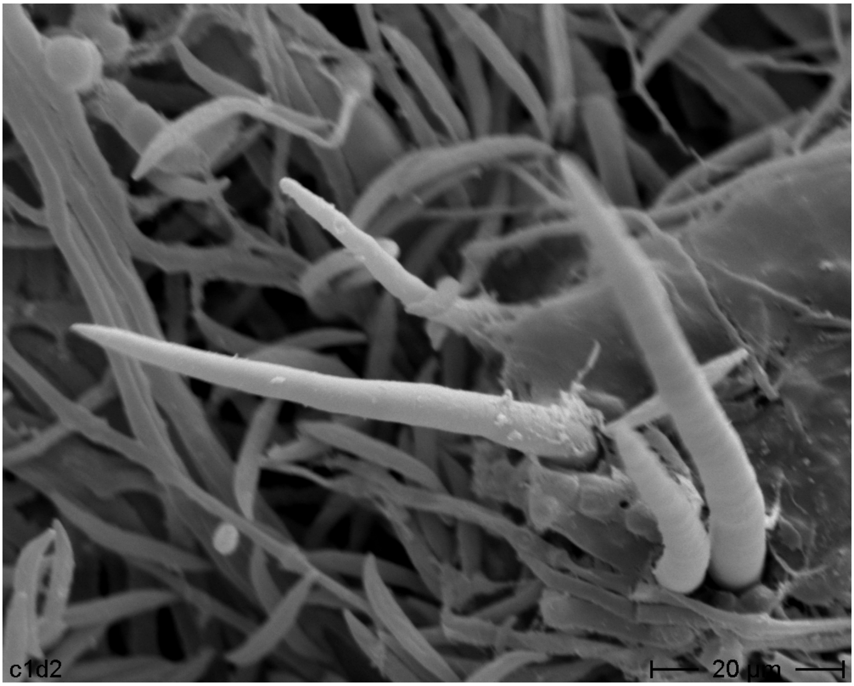

Fig. 3. Acervuli and setae of *C. dematium* in SEM (Photo M. Wróbel)

Fig. 4. Appressoria of *C. dematium* on PDA medium, magnification x500 (Photo E. Zalewska)

The size of 4-days-old colonies growing in the presence of Biochikol 020 PC did not differ significantly in comparison with the size of control colony. The percentage of inhibition of fungus colony growing on the medium with Biochikol at 0.025% and 0.1% concentration was significantly higher in comparison with control colony after 8 day of cultivation. On the other hand at the concentration 0.01% and 0.05% of this preparation no significant differences were observed (Table 3). The colonies of *C. dematium* grown in presence of preparation Biochikol 020 PC, had macro- and micromorphological features like control colonies. They formed acervuli and conidia independently of the concentration of preparation in culture medium. The percentage of growth inhibition of *C. dematium* 4-day-old colonies, on the medium with an addition of grapefruit extract - Bisept 33 SL was significantly higher than control, independently of a.i. concentration in culture medium (Fig. 5). In the presence of 0.1%, 0.2% and 0.3% of the preparation, the percentage of growth inhibition was significantly higher than in the presence of 0.05% of the preparation in the culture medium (Table 3). The inhibition effect of Biosept 33 SL was observed after 8 days of incubation and it was significantly greater than in control. The inhibition effect on the fungus growth at 0.2% and 0.3% concentration of a.i. was significantly higher than at 0.05% and 0.1% concentration of the preparation (Table 3). The colonies of *C. dematium* cultivated on the culture medium with 0.05% Biospet 33 SL formed numerous acervuli and conidia after 8 days, like in control colony. When the concentration of grapefruit extract was 0.1% the fungus formed only a few acervuli and spores. On the other hand, on culture medium with an addition 0.2% and 0.3% grapefruit extract in microscopic studies of mycelium no acervuli and spores of fungus were found. Moreover, degenerative changes in the hyphae of mycelium were observed. The included deformation of cytoplasm, numerous granules, increased vacuoles and the emergence of dark cells in the cross of hyphae (Fig. 6).

Table 3

Impact of the preparations tested on the growth inhibition of *C. dematium* isolate K 426 on the medium containing biotechnical preparations

Concentration **Preparations**	**0.01%**	**0.025%**	**0.05%**	**0.1%**	**control**	**LSD**
Biochikol 020 PC effect after 4 days	2.77a	3.70a	3.70a	-5.55a	0.0a	17.182
effect after 8 days	5.43b	34.77a	3.98b	48.18a	0.0b	27.003
Biosept 33 SL	**0.05%**	**0.1%**	**0.2%**	**0.3%**	**control**	**LSD**
effect after 4 days	44.67b	51.05ab	57.44a	56.37a	0.0a	11.69
effect after 4 days	60.14c	74.43b	85.96a	88.16a	0.0d	2.8065

Values marked with the same letter do not differ significantly, values do not differ significantly from the control $p \leq 0.05$

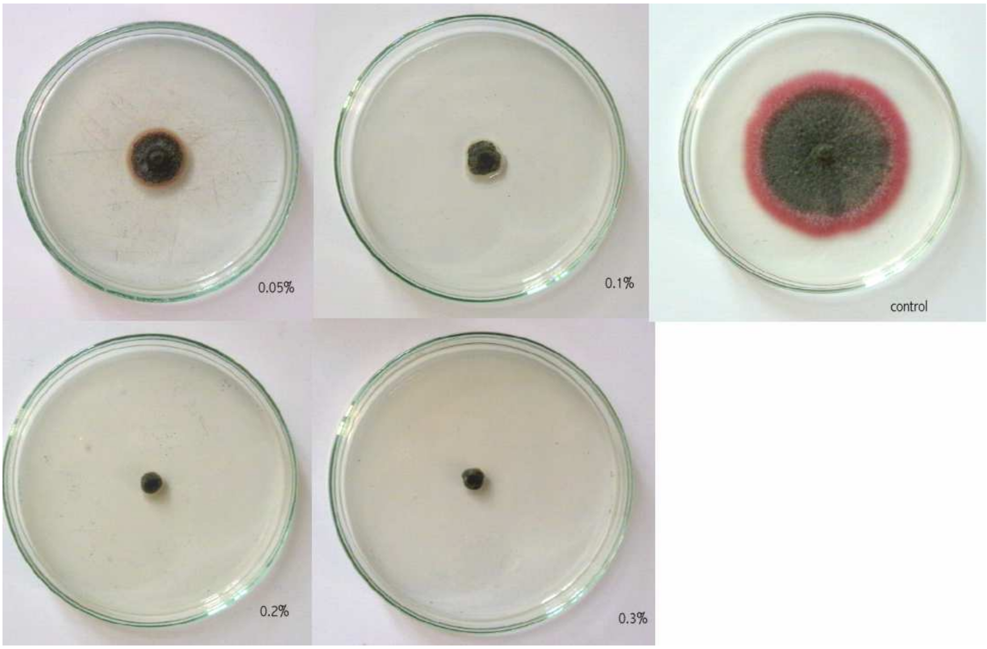

Fig. 5. 8-days-old colonies of *C. dematium* K 425 on the PDA medium with an addition of grapefruit extract (Photo E. Zalewska)

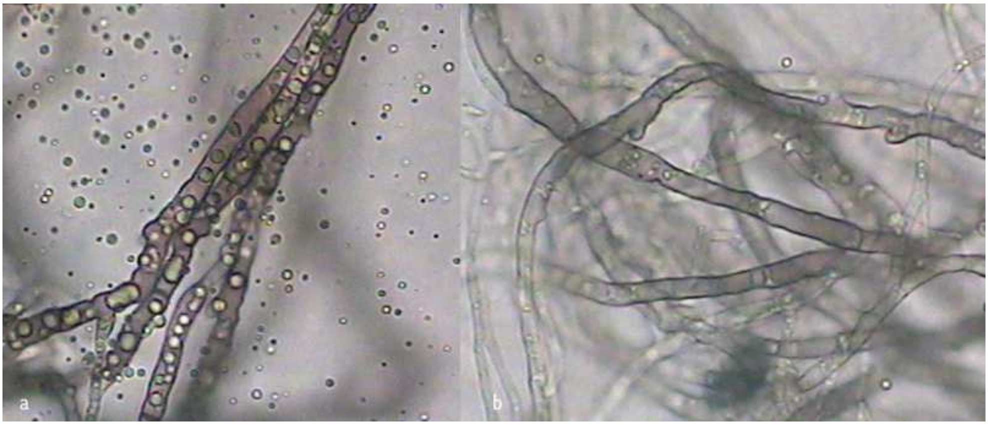

Fig. 6. Degeneration of *C. dematium* hyphae on the PDA medium with an addition of grapefruit extract at concentration 0.2% - a, control hyphae - b, magnification x500 (Photo E. Zalewska)

From among 11 fungicides tested, after 4 days of *C. dematium* cultivation on culture medium with an addition of preparations, only 3 were included in Group III of toxic activity, ie within the substances of moderate fungicidal activity, and 8 in Group IV, ie within the substances with poor fungicidal activity (Table 4). The fungicides applied at the concentration of 1 ppm, except Discus Top 675 WG and Topsin M 500 SC stimulated the growth of the fungus. This effect occurred at 10 ppm in the case of Helm-Cymi 72.5 WP, Kaptan 50 WP, Mildex 711.9 WG, Bravo 500 SC, Tanos 500 WG and Gwarant 500 WG and even at 100 ppm of the latter (Table 4).

Table 4

Impact of fungicides tested on growth inhibition of 4-days-old colonies of *C. dematium*

Fungicides*	Percent of inhibition in relation to a.i. concentration [ppm]		
	1 ppm a.i.	10 ppm a.i.	100 ppm a.i.
III			
Dithane Neo Tec 75 WG	-27.70^{ab}_{C}	2.75_{B}	100.00^{i}_{A}
Helm-Cymi 72.5 WP	-19.40^{abc}_{B}	-27.73^{a}_{B}	100.00^{1}_{A}
Kaptan 50 WP	-14.53^{abcde}_{B}	-7.60^{abcdef}_{B}	77.70^{h}_{A}
IV			
Mildex 711.9 WG	-8.33^{bcd}_{B}	-8.30_{B}	40.20^{efg}_{A}
Amistar 250 SC	-6.95^{bcde}_{A}	11.10^{bcdefg}_{AB}	31.20^{def}_{B}
Discus Top 675 WG	2.73^{d}	24.27^{h}	20.10^{bcde}
Topsin M 500 SC	1.38^{cd}	0^{bcdefg}	29.78^{bcdef}
Rovral Flo 255 SC	-3.45^{cd}	5.50^{bcdefg}	10.37^{bcd}
Bravo 500 SC	-5.55^{cd}	-9.00^{abc}	2.78^{bc}
Tanos 500 WG	-5.50^{cd}	-9.68^{ab}	1.38^{b}
Gwarant 500 SC	-31.73^{a}_{A}	-8.33^{abcd}_{B}	-27.05^{a}_{AB}
Control	0^{cd}	0^{bcdefg}	0^{b}
LSD	21.796		

Capital letters - differences at the studied concentration a.i. of studied fungicide, small letters - differences at the some concentration a.i. of fungicides, values marked with the same letter do not differ significantly, values do not marked differ from others, *fungicides compared according to fungicidal activity group

After 8 days, the effect of the toxicity of fungicides for the fungus was much higher, especially at 100 ppm Amistar 250 SC was included in III and not in IV group of fungicidal activity (Table 5). Moreover, after 8 days of *C. dematium* growth on the culture medium with fungicides, the number of preparations that stimulated fungal growth was reduced, even at 1 ppm (Table 5).

Table 5

Impact of fungicides tested on growth inhibition of 8-days-old colonies of *C. dematium*

Fungicides*	**Percent of inhibition in relation to a.i. concentration [ppm]**		
	1 ppm a.i.	**10 pp. a.i.**	**100 ppm a.i.**
III			
Dithane Neo Tec 75 WG	-9.47^{ab}_{A}	11.15_{B}	100.00^{i}_{A}
Helm-Cymi 72.5 WP	-5.55^{abc}_{A}	-16.17^{a}_{A}	100.00^{1}_{B}
Kaptan 50 WP	-4.45^{abcde}_{A}	-1.15^{ab}_{A}	85.15^{i}_{B}
Amistar 250 SC	4.17^{abcd}_{A}	14.50_{A}	45.20^{def}_{B}
IV			
Mildex 711.9 WG	16.45^{d}_{A}	41.87_{B}	52.77^{fgh}_{B}
Discus Top 675 WG	19.80^{d}_{A}	41.90_{B}	46.33^{defg}_{B}
Topsin M 500 SC	1.67^{abcd}_{A}	-0.02^{abc}_{A}	33.50^{abcd}_{B}
Rovral Flo 255 SC	0.83^{abcd}_{A}	12.80_{AB}	30.33^{abcd}_{B}
Bravo 500 SC	0.33^{cd}	0.57^{abcd}	15.33^{abc}
Gwarant 500 SC	-12.80^{a}_{A}	0.57^{abcd}_{A}	14.12^{ab}_{B}
Tanos 500 WG	10.87^{cd}	7.52^{bcde}	13.38^{a}
Control	0^{abcd}	0^{abc}	0
LSD	17.747		

Capital letters - differences at the studied concentration a.i. of studied fungicide, small letters - differences at the some concentration a.i. of fungicides, values marked with the same letter do not differ significantly, values do not marked differ from others, *fungicides compared according to fungicidal activity group

Table 6

Effect of fungicides on the growth of *C. dematium* colony independently of active ingredients concentration

Fungicides	**Percent of inhibition**	
	after 4 days	**after 8 days**
Amistar 250 SC	11.7833 cde	37.03333 g
Bravo 500 SC	–3.9250 b	5.40833 ab
Discus Top 675 WG	15.7000 def	36.00833 g
Dithane Neo Tec 75 WG	25.0167 f	33.89167 fg
Gwarant 500 SC	–22.3667 a	0.63333 a
Helm-Cymi 72.5 WP	17.6250 def	26.09167 ef
Kaptan 50 WP	18.5250 ef	26.51667 ef
Mildex 711.9 WG	7.8583 cd	21.29167 de
Rovral Flo 255 SC	4.1417 bc	14.65000 cd
Tanos 500 WG	–4.6000 b	10.59167 bc
Topsin M 500 SC	7.3833 cd	11.71667 bc
LSD	10.599	8.6299

Values marked with the same letters do not differ significantly

Analyzing the effect of fungicides irrespective of a.i. concentration, the most toxic after 8 days were Amistar 250 SC, Discus Top 675 WG and Dithane Neo Tec 75 WG (Fig. 7, Table 6).

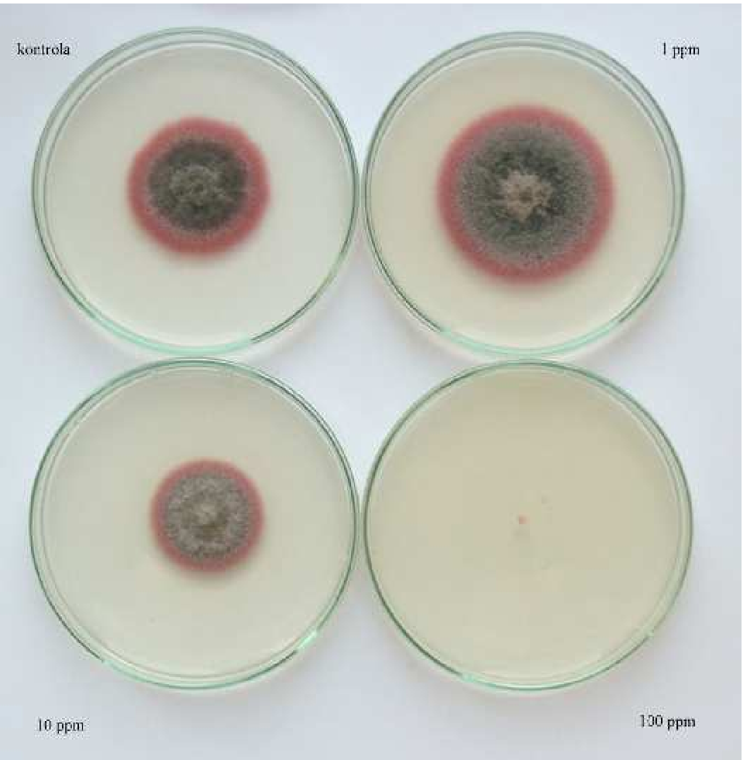

Fig. 7. 8-days-old colonies of *C. dematium* K 425 on the PDA medium with Dithane Neo Tec 75 WG (Photo E. Zalewska)

Table 7

The kind of toxic activity of fungicides on *Coletotrichum dematium*

Fungicides	**Activity**		
	1 ppm	**10 ppm**	**100 ppm**
Amistar 250 SC	++	+	+
Bravo 500 SC	++	++	+
Discus Top 675 WG	+	+	+
Dithane Neo Tec 75 WG	++	+	-
Gwarant 500 SC	++	++	++
Helm-Cymi 72.5 WP	++	++	-
Kaptan 50 WP	+	++	+
Mildex 711.9 WG	++	++	+
Rovral Flo 255 SC	++	+	+
Tanos 500 WG	++	++	+
Topsin M 500 SC	+	+	+

- fungicidal activity, + fungistatic activity, ++ stimulatic activity

The effect on *C. dematium* growth of the most fungicides tested at 100 ppm and biotechnical preparations was fungistatic (Table 7). From among the preparations tested, the effect of only two fungicides Dithane Neo Tec 75 WG and Helm-Cymi 72.5 WP was fungicidal to *C. dematium,* which was shown in total degeneration and death of mycelium as well as the lack of the possibility acervuli and conidia formation.

Discussion

An increasing occurrence of *C. dematium* on caraway since 2005 and the positive results of artificial infection studies [7] confirm earlier suggestions that this fungus should be considered as a potential pathogen of this plant [6]. Detected for the first time in Poland the presence of *C. dematium* on angelica increase the range of host plant of this fungus and indicates its polyphagous character. It can not be excluded that in warm and humid periods of vegetation which are favorable for its occurrence - the thermal optimum 22÷28°C (Zalewska and Machowicz-Stefaniak unpublished) - the harmfulness of the pathogen increases. Because this fungus is not mentioned even among the pathogens in the control programs of vegetable and herbs, all information about the factors affecting the growth and development of *C. dematium* is precious. Basing on the results of present studies, we can conclude that the direct inhibitory effect of Biochikol 020 PC on pathogenic strain of *C. dematium* was insufficient.

Biochicol 020 PC only slightly inhibited the growth of the pathogen, but it did not decrease the intensity of sporulation and did not cause degenerative changes. Such action was shown in relation to other fungi [19-21]. Perhaps indirect effects of Biochikol 020 PC on pathogenic strain of *C. dematium* will be more effective. It results from the fact that chitosan as an elicitor of resistance has the ability to induce multidirectional reactions of resistance in plants, including synthesis of antifungal compounds, hydrolytic enzymes which by hydrolysis of chitin lead to the disintegration of fungi as well as increased activity of peroxidase and hydrogen peroxide [22, 23]. The efficiency of Biosept 020 PC effect in direct contact *in vivo* on pathogenic strain of *C. dematium* was very high. It undoubtedly resulted from the presence of biologically active substances in the preparation, especially endogenous grapefruit flavonoids, glycosides, citrate and lymenon [24]. Especially flavonoids inhibit germination of spores, growth of germ hyphae as well as of vegetative hyphae by damaging the membrane systems and inhibiting the activity of respiratory enzymes [25].

Probably, the above-mentioned mechanisms of effect of these compounds contained in the tested preparation caused significant reduction of the growth, sporulation as well as in degeneration of hyphae of *C. dematium.* The effectiveness of Biosept 33 SL was correlated with the concentration of the bioprepatation. Although already at the lowest concentration tested ie 0.05%, the formation of acervuli by the pathogen was very week, at 0.2% and 0.3% the pathogen did not form these structures, and hyphaes of fungus mycelium were degenerated. Such an effect is observed in the studies of influence of some fungicides on pathogenic fungi [26, 27]. Such interaction of bioproduct is particularly valuable, because wiping mycelium does not allow for the recovery of the pathogen population.

Results of the studies indicate that among 11 tested fungicides, only two, Dithane Neo Tec 75 WG and Helm-Cymi 72.5 WP had fungicidal effect, ie they caused death of the fungus. This property was clearly correlated with the concentration of active ingredient in preparations, but it was not depended on the time effects on the fungal colony.

Extending a high fungicidal activity of these two mentioned fungicides to the eighth day of observation resulted from their fungicidal properties to mycelium of the pathogen, which was shown in present studies. It seems that the element that determines the fungicidal properties of Dithane Neo Tec 75 WG and Helm-Cymi 72.5 WP is mancozeb present in these two preparations. It is especially true because the second element of preparation Helm-Cymi 72.5 WP cymoxanil is present in great quantities in preparation Tanos 50 WG, but this preparation shows only poor inhibiting properties on the fungi growth.

A high ability of preparations Dithane Neo Tec 75 WG and Helm-Cymi 72.5 WP in limiting the growth and development of *C. dematium in vitro* indicates that these preparations can be recommended for further testing in a phytotron and in natural conditions. Similar results were obtained by Shinde and Raut [28] who tested fungicides with a similar chemical compounds in relation to the *C. dematium.* They found that Dithane M-45 inhibited at 100% the growth of the fungus and this fungicide was found to be most effective fungicide among the tested preparations.

On the other hand, Shovan at al [29] indicated that the inhibition of the size of *C. dematium* colony on the culture medium containing Dithane M-45 was not so effective. The high fungicidal activity of macozeb was shown by Machowicz-Stefaniak at al [26] towards the following fungi: *Monilia coryli, Gloeosporium coryli* and *Botrytis cinerea,* and by Zimowska [27] towards *Seimatosporium hypericinum* as well as by Krol [30] towards *Phomopsis viticola.*

The aforementioned authors showed the destructive effect of this preparation not only on spores but on mycelium of the pathogen too. In the present studies the degeneration of hyphae, ie the death of hyphae was caused, besides mancozeb, by azoxystrobin, kresoxim-methyl, thiophanate-methyl and iprodione.

Therefore, the obtained results of present studies showed that the preparations which contain active ingredients mentioned above seem to be good preparations in controlling *C. dematium.* The correctness of this thesis should be confirmed *in vivo* tests.

Analyzing the obtained results, it is noted that *C. dematium* may be a difficult fungus to control. Numerous fungicides tested showed instability in inhibiting the growth of pathogen colonies. Others, especially at lowest concentrations of active substance, stimulated the growth of the pathogen, which was shown by other authors [28]. However, for *C. dematium* and the tested fungicides these properties were noted even at maximum concentration of active ingredients, ie 100 ppm.

Conclusion

1. In view of the high activity of grapefruit extract (Biosept 33 SL) in the direct reduction of *C. dematium* growth and development, this chemical should be considered as potentially useful for testing *in vivo* and controlling the herbs from the *Apiaceae* family.
2. It is advisable to check the indirect effect of Biochikol 020 PC on *C. dematium* ie thought the metabolism of plants with the aim of inducing resistance to this pathogen.
3. The obtained results showed that, the preparation at 0.2% and 0.3% concentration should be taken into account in the studies of Biosept 33SL on *C. dematium in vivo.*
4. Considered the fungicidal effect of fungicides: Dithane Neo Tec 75 WG and Helm-Cymi 72.5 WP on *C. dematium,* their effect on the pathogen should be studied *in vivo.* The effectiveness of Kaptan 50 WP and Amistar 50 SC requires either further testing.

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WYSTĘPOWANIE *Colletotrichum dematium* NA WYBRANYCH GATUNKACH ZIÓŁ ORAZ PREPARATY BIOTECHNICZNE I CHEMICZNE OGRANICZAJĄCE WZROST I ROZWÓJ PATOGENU *IN VITRO*

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Abstrakt: Występowanie mało znanego w Polsce grzyba *Colletotrichum dematium* stwierdzano w latach 2005-2010 na roślinach kminku zwyczajnego oraz w latach 2008-2010 arcydzięgla litwora, uprawianych w okolicach Lublina. Dla patogennego szczepu *C. dematium* K 426 przebadano efektywność wybranych preparatów w ograniczaniu wzrostu i rozwoju tego grzyba. Testowano preparaty biotechniczne: Biochikol 020 PC (chitozan 20 g/dm^3) i Biosept 33 SL (33% ekstraktu z nasion i miąższu grapefruita) oraz 11 fungicydów z różnych grup chemicznych. Metoda polegała na dodaniu preparatu w formie użytkowej do sterylnej pożywki i wszczepieniu na niej inokulum patogenu. Kontrole stanowiły kolonie *C. dematium* na pożywce niezawierającej preparatu. Za kryterium oceny aktywności preparatów przyjęto procent zahamowania wzrostu 4- i 8-dniowych kolonii, rodzaj toksycznego działania, hamowanie tworzenia struktur morfologicznych oraz powodowanie degeneracji grzybni patogenu. Za najbardziej efektywne w ograniczaniu wzrostu i rozwoju patogenu uznano Biosept 33 SL, a z fungicydów Dithane Neo Tec 75 WG oraz Helm-Cymi 72,5 WP.

Słowa kluczowe: *Colletotrichum dematium,* występowanie, Biochikol 020 PC, Biospet 33 SL, fungicydy

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UPTAKE OF ALUMINIUM AND BASIC ELEMENTS, AND ACCUMULATION OF ANTHOCYANINS IN SEEDLINGS OF COMMON BUCKWHEAT (*Fagopyrum esculentum* MOENCH) AS A RESULT INCREASED LEVEL OF ALUMINIUM IN NUTRIENT SOLUTION

POBIERANIE GLINU I PODSTAWOWYCH PIERWIASTKÓW ORAZ NAGROMADZANIE ANTOCYJANÓW W SIEWKACH GRYKI ZWYCZAJNEJ (*Fagopyrum esculentum* MOENCH) W EFEKCIE ZWIĘKSZANIA STĘŻENIA GLINU W POŻYWCE

Abstract: The main aim of the present study was to search for the impact of aluminium (Al^{3+}) on uptake and accumulation of aluminium and basic elements, and on the content of anthocyanins in seedlings of common buckwheat (*Fagopyrum esculentum* Moench). Whole 4-days old buckwheat seedlings or seedlings with excised roots were placed in a growth chamber and exposed to various concentrations of $AlCl_3$ dissolved in Hoagland solution. Aluminium was accumulated in much higher amounts in buckwheat cotyledons and hypocotyls of seedlings incubated after excising roots, than by whole seedlings. High concentration of Al^{3+} in nutrient solution caused the decrease of potassium uptake in buckwheat hypocotyls and cotyledons. The same high Al^{3+} concentration caused significant decline of calcium uptake by hypocotyls, but not by cotyledons. Magnesium level in cotyledons and hypocotyls of buckwheat seedlings without roots treated with Al^{3+} declined, but in case whole seedlings did not undergo such phenomenon. High concentration of Al^{3+} in nutrient solution caused enhanced biosynthesis and accumulation of anthocyanins in hypocotyls, but not in cotyledons of common buckwheat.

Keywords: common buckwheat, aluminium, potassium, calcium, magnesium, manganese, anthocyanins

Although aluminium (Al) is the most abundant metal in the earth's crust, its soluble ionic form (Al^{3+}) shows phytotoxicity, characterized by a rapid inhibition of root elongation [1, 2]. After exposure to Al^{3+}, root growth is inhibited, and other symptoms appear such as

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the reduction of net Ca^{2+} uptake, and blockage of plasma membrane Ca^{2+} channels [2]. In some plant species, aluminium causes also the reduction of reactive oxygen [3]. Moreover, young seedlings are more susceptible to Al^{3+} toxicity than older plants [4].

Aluminium release in acidified soils (pH <5.5) is the main cause of crop yield decreases [5]. It has been estimated that approximately 30% of the world's potential food-producing area is covered by acid soils. These soils are mainly found in regions with high rainfall, where the base cations (Ca^{2+}, Mg^{2+}, K^{+}) have been leached from the soil and replaced by Al^{3+} released from soil mineral weathering. This process is additionally enhanced by the use of ammonium fertilizers and acid rain [1]. In Poland, high concentrations of aluminium in water have been observed mainly in mountain streams. The highest aluminium concentrations were observed during snow melting and after heavy rainfalls [6].

Although Al^{3+} is toxic to plant growth at micromolar concentrations, some plant species show high resistance to the element [7]. Tea, buckwheat, mangroves, some tropical coniferous trees and certain grass species have developed symplastic tolerance mechanisms and accumulate aluminium in their upper part. For example tea can accumulate up to 30 mg Al g^{-1} d.m. [8]. Plants have different mechanisms to alleviate the toxic effect of Al in response to this stress. These defense mechanisms are following: exudation of organic acids from the radical apexes and the subsequent chelation of Al^{3+} in the rhizosphere, and internal production of Al^{3+} chelates in the cells which are later stored in organelles like vacuoles [9]. Al^{3+} ions are taken up by plants mostly through the root system. The major portion of Al^{3+} is transported through apoplast ranging from 30÷90% of the total tissue's content [10].

Interactions between metals are very important for plant growth and development because they determine the availability of metal ions [8]. The interaction between Al^{3+} and Ca^{2+} is an important factor affecting calcium uptake and transport in plants grown in acid soils (pH < 5.5). Increased concentration of Al^{3+} caused a clear declining of Ca^{2+} level in wheat shoots and roots [11]. Al^{3+} also decreased Mg^{2+} accumulation in plants [12]. It is assumed that the main reason for these dependencies is an Al-induced alteration in the properties and structure of membranes. The third element the transport of which is affected by Al^{3+}, is manganese (Mn^{2+}). Low concentration of Al^{3+} in solution (up to 10 μM) had no effect on Mn^{2+} accumulation in roots and shoots, while higher concentrations (up to 100 μM) decreased the accumulation of Mn in shoots of *Vigna unguiculata* [13].

Common buckwheat (*Fagopyrum esculentum* Moench) is highly resistant to Al^{3+} toxicity [14]. Genes encoding transporters for Al-induced secretion of organic acid anions have been identified and characterized [15]. The internal detoxification of Al^{3+} in Al-accumulating plants is achieved by forming Al complexes with organic acids or other chelators and subsequent sequestration of these complexes in vacuoles [16]. It has been reported that in buckwheat oxalate is involved in both external and internal detoxification of Al^{3+} [14]. When buckwheat is exposed to Al^{3+}, oxalate is rapidly secreted from the root tips [17]. Buckwheat also accumulates Al^{3+} at a high level in leaves [14]. Following uptake, Al^{3+} is chelated with internal oxalate in the root cells, forming a stable, non-phytotoxic complex of Al-oxalate. When Al^{3+} is translocated from the roots to the leaves, Al-oxalate is converted to Al-citrate in the xylem. When Al-citrate moves from the xylem to the leaf cells, Al-citrate reconverts to Al-oxalate [16]. About 60% of total Al^{3+} in buckwheat roots is present in the cells as Al-oxalate (1 : 3) [18]. It was moreover found that suppression a leaf's transpiration led to a decrease in the Al^{3+} accumulated by this leaf [19].

The Al-oxalate complex is sequestered in vacuoles in leaves [20]. Interestingly, buckwheat accumulates aluminium in leaves but not in seeds [21]. All these facts are important due to the potential use of buckwheat plants in phytoremediation of metal contaminated soils [22]. The clean up of soils contaminated by metals is a cost-intensive and technically difficult procedure. Therefore the use of plants may have broad perspectives for cleaning metal-contaminated areas.

High concentration of organic acids in leaf tissues is a crucial and widely distributed mechanism that allows plants to alleviate the stress caused by the excess of metallic ions. However, the ability to accumulate high levels of organic acids in tissues is not sufficient for metal tolerance [9]. Plants which accumulate high level of Al^{3+} contain besides organic acids high amounts of flavonoids and phenolics, which can form strong complexes with the metal [9]. Analyses of flavonoids composition, and/or other phenolics, can give additional information on plant response to Al stress.

The main aim of the present study was to search for the impact of Al^{3+} on uptake and accumulation of basic elements important for the physiology of common buckwheat seedlings. It was also studied whether there is a relation between the concentration of Al and anthocyanins in buckwheat seedlings incubated in nutrient solution containing Al^{3+}.

Material and methods

Plant material and growth conditions

Seedlings of buckwheat (*Fagopyrum esculentum* Moench) cv. Hruszowska were used in the study. The seeds were germinated between two layers of wet filter paper [23]. The germination process was carried out in darkness at 24 ±1°C during 4 days. Afterwards, whole buckwheat seedlings or seedlings with excised roots were exposed to various concentrations of $AlCl_3$ dissolved in one fifth Hoagland solution in light/dark conditions in air conditioned growth chamber. This nutrient solution contained the following macronutrients [mM]: KNO_3 (1.0), $Ca(NO_3)_2$ (1.0), $MgSO_4$ (0.4), and $NH_4H_2PO_4$ (0.2); and the micronutrients (µM): Fe-EDTA (20), H_3BO_3 (3.0), $MnCl_2$ (0.5), $CuSO_4$ (0.2), $ZnSO_4$ (0.4), and $(NH_4)_6Mo_7O_{24}$ (1.0). The solution was adjusted to pH 4.5 with 0.1 M HCl. Plants were grown in controlled-environment conditions with a 16/8 h 24/16°C day/night scheme and light intensity of 40 $\mu mol \cdot m^{-2} \cdot s^{-1}$ which was provided by fluorescent tubes.

Determination of anthocyanins

Extraction and measurement of anthocyanins were carried out using the method described by Mancinelli [24], slightly modified by Horbowicz et al [23]. Eight to ten seedlings per one replicate were taken to analyses. Hypocotyls or cotyledons tissues (hand cut into small 2÷3 mm pieces) were extracted with acidified (1% HCl, w/v) methanol for 24 h in room temperature, in darkness with occasional shaking. The extracts were carefully decanted and their absorbance was measured at λ = 530 nm (anthocyanins), and 657 nm (chlorophyll degradation products). The formula A530 - 0.25A657 was used to compensate for the absorption of chlorophyll degradation products at 530 nm. Anthocyanins content was calculated as cyanidin-3-glucoside, which molecular extinction coefficient is equal 29600. Cyanidin-3-glucoside is one of the main anthocyanins in buckwheat tissue [25]. Analyses were carried out for five to eight independent replicates, for hypocotyls and cotyledons separately.

Elemental analyses

Dried and pulverized plant tissues were placed into Teflon vessels, and then 5 cm^3 of 65% nitric(V) acid + 1 cm^3 of 30% H_2O_2 were added. The samples were digested in closed system by Milestone Inc. microwave oven model Ethos-1 at 200°C for 20 minutes according to the producer's procedure [26]. The solutions after digestion were analysed for Al, K, Ca, Mg and Mn content with Perkin-Elmer ICP sequential spectrometer, model Optima 2000 DV. The elements were detected at the following wavelengths [nm]; Al: 396.153, K: 766.490, Ca: 317.933, Mg: 285.213 and Mn: 257.610. The Merck ICP multielement standard solution IV was used for the calibration of spectrometer.

Statistics

The statistical significance of the differences between results was evaluated by means of Student's t-test. The probability values $p \leq 0.05$ was adopted as criterion of significance. The results presented in tables and figure are means ± standard deviation.

Results and discussion

The accumulation of metals from external solution into the shoot comprises of a non-metabolic, passive movement from the external solution to the roots and a transpiration-dependent translocation from the roots to the shoots *via* xylem [27].

Figure 1 contains results on the effect of Al^{3+} concentration in Hoagland nutrient solution on Al content in cotyledons and hypocotyls of whole buckwheat seedlings (A) and of seedlings with excised roots (B), incubated for 7 days. The results have shown that a much higher accumulation of Al occurs in seedlings of common buckwheat incubated after excising their roots. In cotyledons and hypocotyls of seedlings without roots the levels of Al after 7 days' incubation were 10-times and 5-times higher, respectively, than in whole seedlings. In both modes of Al treatment, the concentration of Al in hypocotyls was higher than in cotyledons, yet in case of whole buckwheat seedlings the differences between the amounts of Al in cotyledons and hypocotyls was much greater (Fig. 1). The results suggest also that the roots of buckwheat are important part of efficient defense system against Al toxicity. The results confirm earlier studies in which Al-induced secretion of organic acids by the root system of buckwheat plants has been observed [9, 14, 15]. When buckwheat was exposed to Al, oxalate was quickly secreted from the root tips [17]. Our results confirm also that Al is partly sequestrated in the vacuoles of root system, and therefore cotyledons of whole seedlings accumulate threefold lower amounts of the element than hypocotyls. It is known that following uptake, Al in buckwheat is chelated with the oxalate in root cells, forming a stable, non-phytotoxic complex of Al-oxalate [16]. Thus, only a part of Al^{3+}, *ca* 1/3 of all amount of the uptake element, is transported to cotyledons. Uptake and translocation may vary considerably depending on plant species and metal types. An acropetal decrease in Al concentrations was found in common buckwheat, caused by the low mobility of Al [19].

Table 1 contains results on the effect of Al^{3+} concentration in nutrient solution on the content of potassium (K), calcium (Ca), magnesium (Mg) and managanese (Mn) in cotyledons and hypocotyls of whole buckwheat seedlings and of seedlings with excised roots, incubated for 7 days in Hoagland culture. The results show the importance of the root system for uptake and transport of elements in buckwheat seedlings.

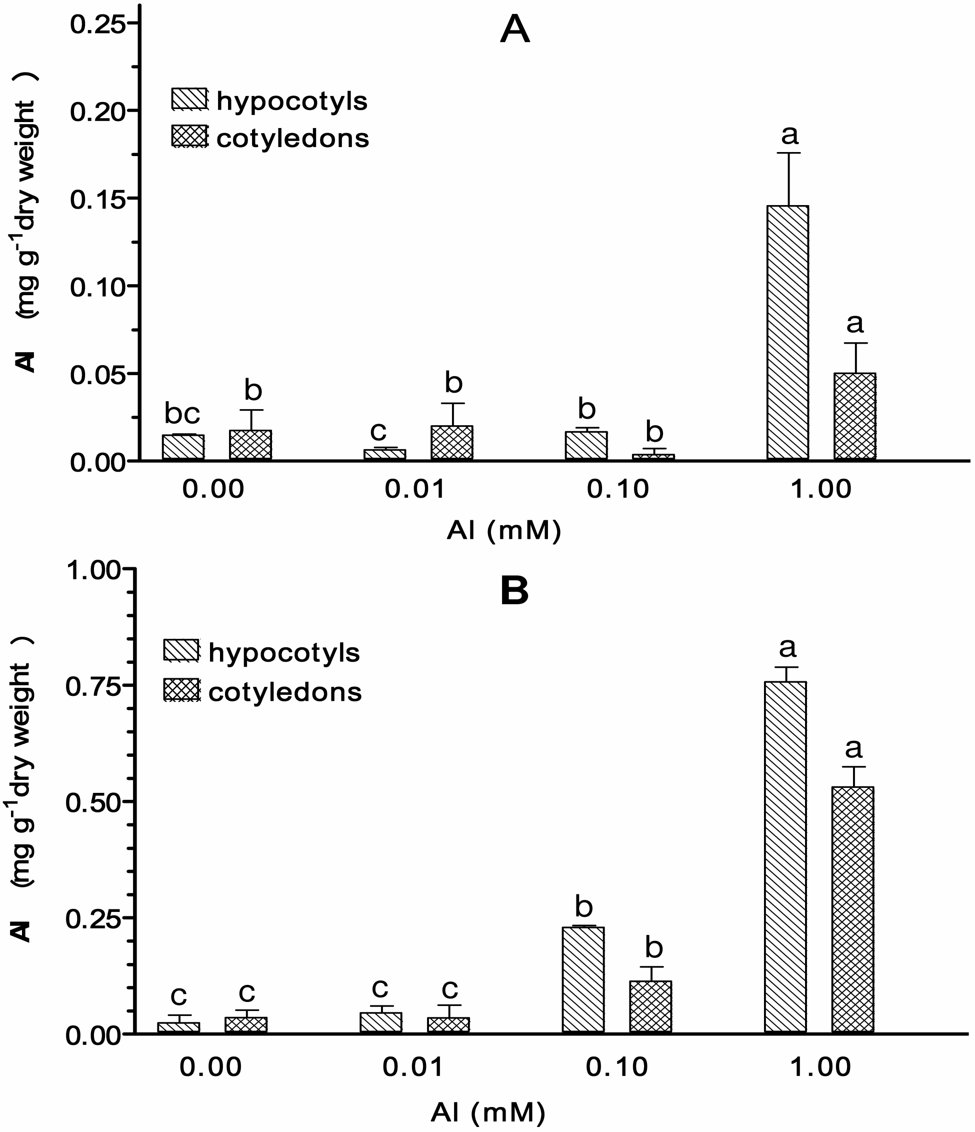

Fig. 1. The effect of Al^{3+} concentration in nutrient solution on aluminium content in cotyledons and hypocotyls of whole buckwheat seedlings (A) and of seedlings with excised roots (B) incubated for 7 days in Hoagland solution. Bar data (means + SD) marked with various letters are significantly different at $p \leq 0.05$ according to t-test - calculated separately for hypocotyls and cotyledons

Cotyledons and hypocotyls of whole seedlings accumulated *ca* three times more K than seedlings with excised roots. In both experimental treatments, only the highest (1 mM) concentration of Al^{3+} caused a significant decline of K content in cotyledons. Also hypocotyls of whole buckwheat seedlings accumulated much lower amounts of K when 1 mM Al was applied. Lower concentrations of Al^{3+} (0.01 and 0.10 mM) did not affect the potassium uptake and accumulation.

Table 1

The effect of Al^{3+} concentration in nutrient solution on the level of basic elements in hypocotyls and cotyledons of whole buckwheat seedlings and of seedlings with excised roots incubated for 7 days (results are means of three replicates ± standard deviation). Results marked with an asterisk (*) are significantly different from control, t-test, $p \leq 0.05$

Analysed element, tissue	**Control (Hoagland solution, no Al^{3+})**	**Al^{3+} concentration in Hoagland solution [mM]**		
		0.01	**0.10**	**1.00**
Whole seedlings				
K, cotyledons	17.77 ±0.88	18.30 ±1.48	18.34 ±0.98	12.52 ±0.59*
K, hypocotyl	36.03 ±4.88	35.13 ±7.61	32.92 ±6.06	15.40 ±0.59*
Ca, cotyledons	6.12 ±1.41	6.07 ±2.33	5.38 ±1.53	6.08 ±2.47
Ca, hypocotyl	18.84 ±0.63	18.21 ±0.55	18.00 ±0.36	13.38 ±0.52*
Mg, cotyledons	4.95 ±0.14	4.98 ±0.01	5.31 ±0.11	5.62 ±0.32
Mg, hypocotyl	2.93 ±0.80	2.85 ±0.79	2.84 ±0.46	1.88 ±0.15
Mn, cotyledons	0.128 ±0.022	0.142 ±0.018	0.136 ±0.015	0.129 ±0.021
Mn, hypocotyl	0.051 ±0.004	0.057 ±0.006	0.061 ±0.003	0.063 ±0.006
Seedlings with excised roots				
K, cotyledons	6.09 ±0.10	5.45 ±0.44	5.00 ±0.29*	4.30 ±0.47*
K, hypocotyl	8.84 ±0.86	6.66 ±0.74	6.84 ±0.50	6.26 ±0.41*
Ca, cotyledons	1.17 ±0.17	1.34 ±0.17	1.03 ±0.18	0.88 ±0.04
Ca, hypocotyl	4.39 ±0.31	3.78 ±0.31	3.88 ±0.26	2.14 ±0.38*
Mg, cotyledons	5.72 ±0.13	4.30 ±0.50*	4.59 ±0.22*	4.25 ±0.03*
Mg, hypocotyl	1.17 ±0.13	0.95 ±0.08	1.04 ±0.04	0.80 ±0.02*
Mn, cotyledons	0.047 ±0.005	0.044 ±0.004	0.044 ±0.004	0.033 ±0.006
Mn, hypocotyl	0.008 ±0.001	0.009 ±0.001	0.009 ±0.002	0.005 ±0.002

K^+ is the most abundant cation in the cytosol, and one of the most crucial for its basic functions, such as osmoregulation, electrical neutralization of anionic groups, and control of cell membrane polarization. Another reason for the cation's essentiality is that some enzymes require K^+ as a cofactor [28]. The plasma membrane is typically more permeable to K^+ than to other ions [29]. It may be assumed that the effect of high Al concentration on uptake, transport and accumulation of potassium is relatively low due to the importance of K^+ physiological functions, and to the plant's membrane permeability.

Similarly to potassium, the accumulation of calcium was much greater in the whole buckwheat seedlings than in the seedlings with excised roots (Table 1). The level of Ca in hypocotyls was *ca* 2-4 times higher than in cotyledons. High concentration of Al (1 mM) decreased the Ca content by almost 30% in relation to controlled hypocotyls of the whole seedlings, and by *ca* 50% in case of seedlings with excised roots. However, regardless of the applied Al concentration, the Ca content was similar in all investigated samples of buckwheat cotyledons. The obtained by us results partly (in case of hypocotyls) confirm the results published by Jones et al [11].

A similar content of magnesium was found in cotyledons of whole seedlings and in cotyledons of the seedlings with excised roots. The incubation of the whole seedlings with Al did not change the level of Mg in the cotyledons and hypocotyls, but it decreased its content in the cotyledons of seedlings with excised roots, regardless of the applied dose of

Al. In the hypocotyls of these seedlings, a *ca* 30% decrease of Mg was noted only under treatment with the highest concentration Al^{3+}, ie 1.0 mM.

Manganese accumulation in the whole buckwheat seedlings as well as in the seedlings with excised roots was affected by concentration of Al^{3+} in nutrient solution. Similarly to magnesium, the content of manganese in cotyledons was much higher than in hypocotyls. Since both elements, magnesium and manganese, play an important role in photosynthetic processes, cotyledons are the major site of their accumulation.

Generally, in our investigations Al^{3+} had a small impact on calcium, magnesium and manganese uptake and accumulation. In earlier studies, the concentrations of calcium and magnesium in buckwheat leaves measured after a 10-days' treatment in 50 μM Al^{3+} were similar in all studied cultivars and did not change as a result of Al^{3+} treatment [30]. However, the Ca and Mg content in roots were reduced while the Al^{3+} concentrations increased [30]. On the other hand, a specific membrane channel for Ca^{2+} transport was found in wheat roots (*Triticum aestivum* L.), which was also permeable to other essential nutrient ions, like Mg^{2+} and Mn^{2+} [31]. The channel was effectively blocked by micromolar concentrations of extracellular Al^{3+} [32]. It seems that the plants of common buckwheat, thanks to the high resistance to Al toxicity are also resistant to disturbances of major essential uptake, like potassium, calcium, magnesium and managanese. An efficient system of Al^{3+} detoxification based on forming various complex molecules containing organic acids is sufficient for protecting the transport system of the given cations through cellular membranes.

According to Barcelo and Poschenrieder [9], plants which accumulate a high level of Al exhibit, alongside organic acids, a high content of flavonoids and phenolics, which can form stable complexes with the metal. Buckwheat tissues are rich in various classes of flavonoids, like glycosides of flavonols, flavones as well as anthocyanins [23, 33, 34]. Accumulation of anthocyanins in hypocotyls of whole buckwheat seedlings was Al-dependent (Table 2). A significant dependence was noted after 7 days' incubation with 0.10 and 1.00 mM of Al^{3+}. No such relation was found in case of anthocyanins and Al in buckwheat cotyledons. In cotyledons, the content of anthocyanins was lower after 7 days of experiment duration, than after 3 days, and the level was not affected by Al. A similar observation was made in case of applying Al^{3+} to buckwheat seedlings with excised roots (Table 3). The highest concentration of Al^{3+} caused clear increase of anthocyanins level in hypocotyls after 3 and 7 days of treatment duration. Cotyledons of these seedlings contained similar levels of anthocyanins, independently to the used dose of Al. It suggests that there exists, probably, an additional mechanism in buckwheat hypocotyls of Al detoxification based on forming complex compounds between anthocyanins and aluminium cations. In fact, several complexes of the like (ie metal-antocyanins) were found in plants [35]. For example, the colour change of hydrangea (*Hydrangea macrophylla*) has been suggested to be caused by free Al^{3+} complexation with anthocyanins [36].

The increased synthesis of anthocyanins in buckwheat seedlings under Al treatment can be caused by the metal's influence on the uptake of phosphates (P). Al^{3+} interference with P uptake might result in P deficiency in plants grown on acid soils or in nutrient solutions [37], which in turn enhances the accumulation of anthocyanins, as recently was found by Mioduszewska et al [38].

Table 2

The effect of Al^{3+} concentration in nutrient solution on the level of anthocyanins [$\mu g \cdot g^{-1}$ f.m.] in hypocotyls and cotyledons of whole buckwheat seedlings incubated for 3 or 7 days (results are means of 5 to 8 replicates ± standard deviation). Results marked with an asterisk (*) are significantly different from control, t-test, $p \leq 0.05$

Time of incubation [days]	**Control (Hoagland solution, no Al^{3+})**	**Al^{3+} concentration in Hoagland solution [mM]**		
		0.01	**0.10**	**1.00**
Hypocotyls				
3	327.6 ±36.2	318.2 ±34.2	341.0 ±39.6	356.2 ±31.3
7	451.0 ±66.4	546.9 ±87.0	545.6 ±42.4*	716.3 ±84.8*
Cotyledons				
3	221.6 ±43.1	229.3 ±34.9	236.5 ±41.3	216.1 ±29.7
7	156.9 ±61.2	114.9 ±34.6	107.4 ±33.9	142.5 ±27.5

Table 3

Effect of Al^{3+} concentration in nutrient solution on the level of anthocyanins [$\mu g \cdot g^{-1}$ f.m.] in hypocotyls and cotyledons of buckwheat seedlings with excised roots, incubated for 3 or 7 days (results are means of 5 to 8 replicates ± standard deviation). Results marked with an asterisk (*) are significantly different from control, t-test, $p \leq 0.05$

Time of incubation [days]	**Control (Hoagland solution, no Al^{3+})**	**Al^{3+} concentration in Hoagland solution [mM]**		
		0.01	**0.10**	**1.00**
Hypocotyls				
3	394.1 ±35.9	435.2 ±42.3	466.5 ±61.3	481.5 ±40.2*
7	584.3 ±61.1	598.3 ±58.8	635.1 ±60.5	782.1 ±84.1*
Cotyledons				
3	292.3 ±25.3	289.7 ±20.9	314.9 ±33.2	333.0 ±46.7
7	168.4 ±56.2	266.0 ±38.4	216.9 ±26.7	246.0 ±46.1

Conclusions

1. Aluminium was accumulated in much higher amounts in buckwheat cotyledons and hypocotyls of seedlings incubated after excising roots, than by whole seedlings. The results confirm known fact that in the buckwheat roots pose efficient system of Al detoxification.
2. High concentration of Al^{3+} in nutrient solution caused the decrease of potassium accumulation in buckwheat hypocotyls and cotyledons, and caused significant decline of calcium uptake by hypocotyls, but not by cotyledons.
3. The highest concentration of Al^{3+} in nutrient solution caused increase of anthocyanins level in hypocotyls. It suggests that there exists an additional mechanism of aluminium detoxification based on forming complex compounds between anthocyanins and aluminum cations.

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POBIERANIE GLINU I PODSTAWOWYCH PIERWIASTKÓW ORAZ NAGROMADZANIE ANTOCYJANÓW W SIEWKACH GRYKI ZWYCZAJNEJ (*Fagopyrum esculentum* MOENCH) W EFEKCIE ZWIĘKSZANIA STĘŻENIA GLINU W POŻYWCE

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Abstrakt: Celem prezentowanych badań była ocena wpływu glinu (Al^{3+}) na jego pobieranie i akumulację oraz podstawowych pierwiastków, a także na zawartość antocyjanów w siewkach gryki zwyczajnej (*Fagopyrum esculentum* Moench). Całe 4-dniowe siewki lub siewki z odciętymi korzeniami rosły w komorze wzrostu na pożywce Hoaglanda, zawierającej różne stężenia $AlCl_3$. Glin był nagromadzany w znacznie większych ilościach przez liścienie i hipokotyle roślin gryki pozbawionych systemu korzeniowego w porównaniu do całych siewek. Duże stężenie Al^{3+} w pożywce powodowało hamowanie pobierania potasu przez liścienie i hipokotyle gryki. Takie samo stężenie Al powodowało obniżenie pobierania wapnia przez hipokotyle, ale nie przez liścienie. Poziom magnezu w liścieniach i hipokotylach siewek gryki pozbawionych systemu korzeniowego obniżał się pod wpływem jonów Al^{3+}, ale takie zjawisko nie wystąpiło w roślinach mających system korzeniowy. Wysokie stężenia Al^{3+} w pożywce powodowało zwiększoną biosyntezę i akumulację antocyjanów w hipokotylach, ale nie w liścieniach gryki zwyczajnej.

Słowa kluczowe: gryka zwyczajna, glin, potas, wapń, magnez, mangan, antocyjany

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ORGANIC MATTER AS THE GREATEST BIOENERGY POTENTIAL OF SOILS - SURFACE ACTIVITY OF HUMUS SUBSTANCES

MATERIA ORGANICZNA GLEB JAKO NAJWIĘKSZY POTENCJAŁ BIOENERGETYCZNY GLEB - AKTYWNOŚĆ POWIERZCHNIOWA SUBSTANCJI HUMUSOWYCH

Abstract: Humus compounds originating from typologically differentiated soils, ie a podsol and a chernozem was characterized. The paper presents the results of determinations of elemental composition and also of important physicochemical parameters determining the structure and the surface activity, such as total specific surface area, outer specific surface area, molar energy of adsorption, and microporosity. High differences in the sorption of nitrogen and water vapour are the result of the complex mechanism of adsorption with both polar and polar adsorbates. The microstructure of humus acids, generated under moist condition, is unstable and upon drying (irrespective of the method of drying) of the preparation the microstructure disappears, structural collapse takes place, and it then occurs in a compact and non-porous form, inaccessible to both mercury and polar adsorbated (nitrogen), as was shown by measurements of nitrogen adsorption on the preparation and by porosimetric measurements.

Keywords: humic acids, β-humus, elemental composition, isotherms of water vapour adsorption, specific surface area, molar energy of adsorption, microporosity

The organic matter of soils is the greatest bioenergy potential of soils, determining the favourable nature of the whole complex of soil properties related with the fertility and productivity of soils. The primary component of organic matter (85÷90%) are decayed parts of plant organisms, both those identifiable macroscopically and in the colloidal form, which are referred to as humus substances. The main components of humus substances, in turn, are humic and fulvic acids and humins, which differ in their structure, molecular mass, elemental composition, content of functional groups, and surface activity. Their complex polymeric structure determines the biological, chemical and physical properties in soils, which are the determinants of the functions they play in ecosystems [1].

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In view of the enormous role of humus compounds in soils, the control and prediction of the status of humus, in both the quantitative and qualitative aspects, is a very important problem. There are numerous studies [2-4] concerned with the characterization of humus compounds originating from soils subjected to strong anthropogenic effect (fertilization, crop rotation, tillage, pollution), while relatively few are concerned with characterizing humus compounds from natural forest areas.

The objective of this study was to characterize humus compounds originating from model forest soils, differing in their soil-forming processes, ie a podsol and a chernozem. Intensive processes of weathering of the mineral phase and of transport of the resultant products into the depth of the soil profile predominate in podsols. In those processes, a considerable role is played by accumulated in horizon O acid easily-soluble humus compounds, mainly fractions of fulvic acids, formed as a result of decomposition of acidophilic forest vegetation (spruce, pine, blueberry, heather, etc.) with the participation of fungi. For this reason, the nature of humus compounds from podsols, and their surface activity and microstructure, will be different than of humus compounds from chernozem where biological processes predominate, resulting in a considerable influx of organic matter to the soil substrate.

To determine the physicochemical nature of the humus fractions (humic acids and β-humus fractions of fulvic acids), their elementary composition was determined (in % by weight) and the quantitative C/N and C/H ratios were calculated as the fundamental analyses necessary for the characterization of the compounds [5-10]. Also determined were the surface activity and the microstructure. The surface activity was determined on the basis of analysis of the calculated parameters characterizing the structure and sorption, such as specific surface area and molar energy of adsorption [5, 6, 11-14, 16-18]. The microstructure was characterized on the basis of results of the outer specific surface area determined with the method of low-temperature adsorption of nitrogen, and of porosimetric analyses [5, 12, 13, 17, 18].

The differences in the physicochemical nature of humus compounds from podsol and from chernozem are due to heterogeneity and to the conditions under which they were formed.

Materials and methods

The material for the study was composed of humus acids fractions (humic acids and β-humus fraction of fulvic acids) originating from the humus-ferrous horizon of a pine forest podsol and from the humus horizon of a natural forest chernozem.

For the study the author selected soils differing from each other in order to emphasize the differences between the chemical nature and the degree of condensation of the aromatic nucleus of their humus acids. The complexity of structures of soil humus substances is related with soil type and use. The structure of humus substances from a podsol is characterised by the lowest degree of condensation of the aromatic nucleus and the least polymerisation, while that of humus substances from a chernozem have the opposite characteristics. The notably different molecular structure of humus acids from a podsol and a chernozem is largely a result of the character of the soil-formation process, so different in those types of soils. Physicochemical properties of podsol and chernozem were presented in Tables 1 and 2 [13].

Table 1

Physicochemical properties of podsol [13]

Horizon	Textural class [%]			pH		C [%]	$CaCO_3$ [%]
	2.05÷0.05 mm	0.05÷0.0002 mm	< 0.002 mm	KCl	H_2O		
O	92	6	1	3.2	4.2	0.88	-
Es	96	3	1	3.8	4.8	0.18	-
Bhs	95	2	3	3.5	4.1	0.54	-
Bs	97	2	1	4.4	5	0.26	-
C	97	2	1	4.4	5.1	-	-

Table 2

Physicochemical properties of chernozem [13]

Horizon	Textural class [%]			pH		C [%]	$CaCO_3$ [%]
	2.05÷0.05 mm	0.05÷0.0002 mm	<0.002 mm	KCl	H_2O		
Ah_1	15	78	7	6.6	6.7	2.33	0
Ah_2	13	70	17	6.55	6.85	0.99	0
Ah_2B	15	72	13	7.15	7.75	0.56	0.2
BK	13	68	19	7.25	7.5	0.44	1.6
CK	14	70	16	7.6	7.6	0.13	10.1

Humic acids were isolated from the soils studied using the Schnitzer's method [13-16, 19], in the following way: a soil sample was flooded with 0.5 M solution of NaOH at a ratio of 1 to 10, and then left for 24 hours in a nitrogen atmosphere, at room temperature, stirred now and then. Conducing extraction in the nitrogen atmosphere is necessary to avoid redox processes, to which quinone and phenol systems, as well as their derivatives present in the aromatic core of humic acids particles, are highly sensitive. Humic acids extracted in this way, were then separated from the non-soluble residue by centrifuging. Next, the solution was acidified to pH 2 using 6 M solution of HCl, and left for till the following day. The sediment of humic acids was separated from the solution of fulvic acids by centrifuging. Humic acids sediment obtained was purified by shaking with HCl-HF mixture for 12 hours. The solution was separated from the sediment by centrifuging. The operation was repeated three times, and then the humic acid preparations were washed with distilled water until reaction with chlorides was eliminated.

The acid filtrate of fulvic acids was used to precipitate β-humus using the Stevenson's method [13-16, 20]. For this purpose, the solution was alkalised to pH 4.8 using 5 M NaOH and 0.1 M NaOH. The resulting sediment of β-humus was centrifuged from the residue and washed twice with distilled water.

Preparations of humous acids, in the form of a sediment after purification and filtration, to avoid oxidation effect, as follows: they were placed on crystallizers and, under vacuum (12 mm Hg), their moisture content was lowered to the level corresponding to a pressure of $p/p_0 = 0.5$. Samples were initially dried, and then placed in an exsiccator, over concentrated sulphuric acid for further gradual drying.

The preparations obtained were subjected to the following physicochemical examinations:

– Ash content was determined by burning the preparations in a muffle furnace at a temperature of 800°C.
– Elementary composition (C, H, O, N) on a Perkin Elmer type 2400 analyser C/H and C/N rations were calculated.

- The adsorption isotherms of water vapour were measured using the gravimetric method at temperature T = 20°C (Fig. 1). Before the adsorption measurement, the samples were gently ground and dried in a vacuum chamber with the concentrated sulphuric acid until the sample masses reached constant values. The subsample of about 3 g was put into the glass vessel and was placed over sulphuric acid solutions of stepwise decreasing concentrations (to increase of the relative water vapour pressure ie to determine the adsorption branch of isotherm) and next over sulphuric acid solutions of stepwise increasing concentrations (to decrease of the relative water vapour pressure ie to measure the desorption branch of isotherm). The sample was equilibrated with water vapour during two days. The amount of adsorbed water vapour was computed as the difference between the weight of the sample after the equilibration and the dry sample (dried in an oven at 105°C). The adsorption measurements were replicated three times at temperature T = (20 ±0.5)°C. Twenty levels of relative pressure were selected in the range from 0.015 to 0.95. The variation in replicated data did not exceed ±5% at the lowest vapour pressure and ±1% at the highest vapour pressure. The average values at each pressure level were used to obtain the specific surface areas [21-23].

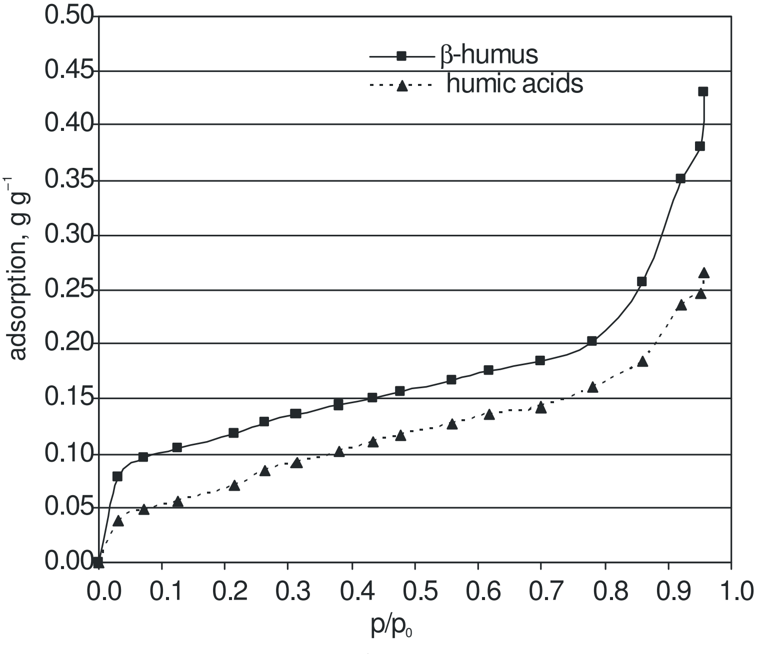

Fig. 1. Isotherms of adsorption of humic acid and β-humus

- The specific surface area of preparations (humic acids and β-humus) was evaluated from adsorption isotherms at temperature (T = 20°C) in the BET range of relative water vapour pressure ($0 < p/p_0 > 0.35$), using the *Brunauer-Emmett-Teller* (BET) method [12-14, 16-18, 24]. The experimental data have been described using the BET equation. The parameters of this equation ie monolayer capacity N_m, and constant C_{BET}, as well as the standard error square, R^2 were estimated from the linear form of the BET equation (Table 5).

Table 5

Parameters of adsorption isotherms for mono-layer of the adsorbent, such as the, monolayer capacity N_m, constant C from the BET equation and standard error square R^2

Sample	**Mono-layer-capacity N_m**	**Constant C from the BET equation**	**Standard error square R^2**
Humic acid podsol	0.070	23.1	0.990
Humic acid chernozem	0.056	14.9	0.983
β-humus podsol	0.090	171	0.999
β-humus chernozem	0.090	36.9	0.992

This procedure is described by the Polish standard PN-Z-19010-1 (1997) [25] for measuring the surface area of soils.

Molar energy of water vapour adsorption was determined with the help of the water vapour adsorption isotherms at 20 and 40°C for a monolayer of every preparations adsorbent studied [5, 6, 13, 17].

The molar energy of adsorption for the monolayers (m) was calculated according to the formula for molar enthalpy (H^S):

$$\Delta a H_m^S = 2.3038\, R_0 \, \mathrm{tg}\alpha$$

where R_0 - gas constant = 8.3144 J $K^{-1}mol^{-1}$.

Data from the calculations were compared with the value of molar enthalpy of evaporation L = ΔH_{373}^0 = 40.72 kJ mol^{-1} [5, 6, 13, 16, 17, 26, 27].

The size of the external surface was determined using the method of the low-temperature adsorption of nitrogen [11, 13, 28, 29].

Microstructure was assessed on the basis of determinations of microporosity distribution with the method of mercury porosimetry [10, 12, 13, 27, 29-31].

The above examinations will provide an answer to the question whether the differences in the molecular structure, and primarily in the degree of condensation of the aromatic nucleus, will affect the physicochemical activity of the surface of the preparations.

Results and discussion

In the analysis of the obtained results of determinations for humus compounds from podsol and chernozem, the primary concern was to identify the differences in their physicochemical nature and to observe whether the soil-formation process has a modifying effect on the humus compounds. The results can be considered as model ones and they can be used for comparisons with the physicochemical properties of humus compounds from soils subjected to a strong anthropogenic effect, such as crop rotation, fertilization, pollution, tillage, etc.

Considerable differences can be observed in the degree of contamination of the humus acids preparations under study, especially in the preparations of β-humus. The β-humus fraction from the podsol showed a higher ash content (35.13%) as compared with the sample from the chernozem (27.17%) (Table 3), which is related to the higher content of iron, aluminium and other contaminants in the studied horizon of that soil profile. One can assume that β-humus means permanent organic-mineral bonds [13]. Also the analysis of the elementary composition (in percentage by weight) of the humus compounds under study showed a considerable differentiation in their composition (Table 3).

Table 3

Elementary composition [%] of dry mass cinderless and ash of humus compounds under study

Sample	**Ash content**	**C**	**H**	**N**	**O**	**C/H**	**C/N**
Humic acid - podsol	5.25	$\frac{56.50}{40.53}$	$\frac{4.60}{39.08}$	$\frac{3.00}{1.87}$	$\frac{35.90}{19.03}$	12.3	19.0
Humic acid - chernozem	3.98	$\frac{55.90}{34.80}$	$\frac{6.40}{47.40}$	$\frac{2.80}{1.50}$	$\frac{35.00}{16.30}$	8.8	20.0
β-humus - podsol	35.13	$\frac{45.40}{29.90}$	$\frac{5.80}{45.90}$	$\frac{1.50}{0.87}$	$\frac{47.30}{23.40}$	7.9	30.3
β-humus - chernozem	22.17	$\frac{32.90}{22.30}$	$\frac{5.70}{46.30}$	$\frac{4.20}{2.50}$	$\frac{57.10}{29.00}$	5.7	7.8

In the numerator - in percentage by weight
Denominator - in atomic percentage (per by mass without ash)

Humic acids have a considerably higher content of C as compared with β-humus fractions, while in the case of H a reverse relation was observed. The content of N in humic acids falls within the range of 3%, and that of O - of 36%. Differentiated and opposite content of nitrogen was observed in the case of the β-humus preparations. The β-humus fraction from the podsol contained 1.5% of N, while that from the chernozem - 4.2%. Differentiated elementary composition determines the existence of various values of the quantitative ratios of C/N and C/H which are used for the characterization of the variability of humus acids. The C/H ratio varies and provides an index of aromaticity, while the C/N ratio determines the degree of "naturity" of humus acids [4-6, 10, 13, 31]. Humic acids have a higher C/H ratio, with values within the range of 12.3÷8.8%, as compared with β-humus preparations. This indicates weaker aromatisation of the β-humus preparations, which is related to their lower C content and somewhat higher H content compared with humic acid preparations. Preparations of β-humus, although they contain basic units with a structure similar to that of humic acids, have weakly formed aromatic nucleus. As to the C/N ratio in humic acids, its values vary from 19 to 20.0. A significantly different, and at the same time highly varied C/N ratio was observed in the preparations of β-humus. For the podsol the C/N ratio value was 30.3, while for the chernozem - 7.8. This indicates slow humification and mineralization of organic substance, producing relatively low amounts of mineral nitrogen (1.5% N for β-humus from the podsol). β-humus from the chernozem showed a lower value of C/N ratio (7.50, which indicates strong humification and mineralization leading to the generation of greater amounts of nitrogen (4.2%)). The C/N ratio decreases with increasing degree of humification. This is due to the faster reduction of the amount of carbon as compared with nitrogen in decomposing debris and residues.

Humus compounds from the podsol and the chernozem differ in their molecular structure, and especially in the degree of condensation of their aromatic nucleus. Humus compounds from the podsol are characterized by the lowest degree of condensation of the aromatic nucleus and by the weakest polymerisation, while those from the chernozem - by the highest. These properties have a strong effect on the physicochemical activity of the surface of the preparations [13, 18, 26, 32]. Hence, the physicochemical properties of the preparations studied were characterized (Table 4).

Table 4

Surface properties of humus compounds (humic acids and β-humus)

Sample	**Specific surface area [m^2 g^{-1}]**	**Molar energy of adsorption [KJ mol^{-1}]**	**External surface area [m^2 g^{-1}]**	**Mean pore diameter [µm]**
humic acid podsol	238	58.6	1.0	3.0732
humic acid chernozem	201	57.4	0.98	3.8241
β-humus podsol	319	65.0	34.00	0.0063
β-humus chernozem	329	66.1	33.85	0.0060

Characterizing the parameters presented (Table 4) one can state that humic acid from the podsol has a greater specific surface area (238 m^2 g^{-1}) when compared with humic acid from the chernozem (201 m^2 g^{-1}). The specific surface area of β-humus is considerably greater than that of humic acids. As to the molar energy of adsorption, no greater differentiation was observed in the values of that parameter in the case of humic acids (58.6÷57.4 kJ mol^{-1}), but for β-humus it was much more pronounced at 65÷121 kJ mol^{-1}. The presented values of the specific surface area and the molar energy of adsorption reflect the aforementioned differences in the molecular structure, namely the differences in the degree of condensation of the aromatic nucleus of humus acids from podsol and chernozem. Humic acids from the podsol, due to the predominance of lateral chains in their molecules, are characterized by greater hydrophilicity than humic acids from chernozem, whose molecules are dominated by the aromatic nucleus. Similar relations occur between the humic acids and β-humus which, in turn, compared with the humic acids, has in its chemical structure much more lateral chains with weaker developed aromatic nucleus. Those proportions in the molecular structure affect the values of the specific surface area and of the molar energy of adsorption [13, 16, 26, 33]. A β-humus from the podsol showed a very high molar energy of water adsorption (121 kJ mol^{-1}), which may be related to the presence of contaminants and to the occurrence of specific adsorption, characterized by a higher energy. On the basis of the measurements of specific surface area and molar energy of adsorption one can state that humic acid from the podsol displayed a greater activity when compared with that of humic acid from chernozem. Also, when compared with humic acids, β-humus had a greater surface activity, stronger sorptive properties, much more active functional groups that act as adsorption centres and have a greater capacity to adsorb adsorbate molecules on their surface, and hence its greater specific surface area.

In order to acquire a deeper knowledge of the physicochemical properties of humus acids, also the outer surface was determined, with the method of low-temperature nitrogen adsorption, as a result of which it turned out that the outer surface of humic acids was very low, less than 1 m^2 g^{-1}, while that of β-humus was approximately 34 m^2 g^{-1}. The considerable differences in surface area values measured with water vapour and nitrogen induce the need of analysing the mechanism of adsorption. In the case of apolar adsorbates (nitrogen), adsorption takes place on the external surfaces, and it is probably the low energy of adsorption that does not permit the adsorbate molecules to penetrate into the material. We are dealing here with the outer specific surface area. Hence, the specific surface area as measured with nitrogen is very small, which indicates that the formed structure of humus acids is unstable and when the preparation is freeze dried (which was necessary with the method adopted) the structure *collapses*, ie the pores shrink, preventing nitrogen or mercury from penetrating into the material. This is a non-porous, compacted material. This means that the formed microstructure of humus acids is unstable under natural conditions and is water-related; hence the specific surface area as measured with water vapour is much greater, as adsorbate (water vapour) molecules penetrate to the polar functional groups (acting as adsorption centres) and are adsorbed on those groups. This is related with a relatively high energy of adsorption in the case of a polar adsorbate, such as water.

The differences in the microporosity of humic acids and β-humus were also confirmed by porosimetric analyses (Table 4), though no differences were shown between the humum compounds originating from the podsol and from the chernozem. The value of the mean pore diameter was similar for all the humic acid preparations under study. Humic acid from the podsol 3.073 μm, and humic acid from the chernozem 3.824 μm. This is external porosity related to the degree of grinding of the preparation concerned. Humic acids are materials that are totally non-porous and display no internal microporosity. Preparations of β-humus from podsol and chernozem have similar values of prediameter 0.0063 μm for the podsol and 0.0060 μm for the chernozem. The preparations of β-humus, apart from external porosity, show also the presence of internal microporosity. The porosity originates probably from contamination, or else one can say that the β-humus fraction is a permanent organic-mineral complex characterized by a lower degree of aromatisation, greater number of lateral chains, stronger sorptive properties, greater activity and higher ion exchange capacity.

The differences in surface activity and microstructure between humic acids and β-humus improved also shapes of isotherms of water vapour adsorption. The isotherms of water vapour adsorption in 20°C on humus substances (humic acids and β-humus are presented in Fig. 1). The shape of the presented isotherms belong to the second type of the BET classification [17, 18, 21, 23], and is typical for physical adsorption of gases. The fraction of β-humus had a clearly different isotherm shape than the humic acids, and proves the differentiated microstructure of that fraction. These changes are probably correlated with the different ash content levels in the preparations (Table 3). The isotherms of water vapour adsorption on humic acids, have a very similar shape and are close in shape to the adsorption curve of β-humus (Fig. 1). The shape of the isotherm of water vapour adsorption on fraction of β-humus is some what is different from those on humic acids, especially in the range of relative pressure from 0.72÷0.92 p/p_0, which could be related to the occurrence of capillary condensation. It also caused a decrease in the amount of adsorbed water vapour on the humic acids. Comparison of the adsorption curves indicates that the fraction of β-humus adsorbs much more water vapour on those humic acids.

Conclusions

The process of soil formation significantly affects the differentiation of the quality of humus compounds. Fractions of humus compounds from chernozem and from podsol significantly differ in the molecular structure, degree of condensation of the aromatic nucleus, polymerisation, and physicochemical nature.

Surface phenomena are the principal determinants of the physicochemical properties and play an important role in agrophysical sciences. They provide the basis for the formulation of conclusions concerning the role of humus compounds in ecosystems.

The results of measurements of specific surface area and molar energy of adsorption, showed that humic acids and fulvic acid fraction of β-humus from podsol are characterized by a greater surface activity as compared with the same fractions from chernozem. High differences in nitrogen and water vapour sorption on preparations of humus acids indicate a complex and different mechanism of adsorption with polar and apolar adsorbates on those substances.

In the case of β-humus, the internal microporosity showed by mercury porosimetry probably originates from inorganic contaminants or else is the effect of permanent bonding of that fraction with the mineral part of the soil.

Differences in the molecular structure of hums acids, ie of humic acids and ß-humus and their level of inpurities have a considerable influence on the microstructure of these substances.

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MATERIA ORGANICZNA JAKO NAJWIĘKSZY POTENCJAŁ BIOENERGETYCZNY GLEB - AKTYWNOŚĆ POWIERZCHNIOWA SUBSTANCJI HUMUSOWYCH

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Abstrakt: W pracy przedstawiono charakterystykę kwasów humusowych pochodzących z gleb zróżnicowanych typologicznie, bielicy i czarnoziemu. Określono skład pierwiastkowy oraz ważne parametry fizykochemiczne determinujące strukturę oraz aktywność powierzchniową: izotermy adsorpcji pary wodnej w 20ºC, powierzchnię właściwą całkowitą, powierzchnię właściwą zewnętrzną, molową energię właściwą, pojemność monowarstwy, stałą C z równania BET, kwadratowy błąd standardowy oraz mikroporowatość. Duże różnice w sorpcji azotem i parą wodną są wynikiem mechanizmu adsorpcji adsorbatem polarnym i apolarnym. Mikrostruktura kwasów humusowych kreowana przez wodę jest niestabilna i zależy od metody suszenia. Przy jej suszeniu następuje załamanie się struktury (*collapse*) i występuje ona w formie zbitej, nieporowatej, niedostępnej zarówno dla rtęci, jak i też dla adsorbatów apolarnych, co wykazały pomiary adsorpcji i desorpcji azotu oraz pomiary porozymetryczne.

Słowa kluczowe: kwasy huminowe, β-humus, skład pierwiastkowy, izotermy adsorpcji pary wodnej, powierzchnia właściwa, molowa energia adsorpcji, mikroporowatość

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EFFECT OF ORGANIC MATTER FROM VARIOUS SOURCES ON YIELD AND QUALITY OF PLANT ON SOILS CONTAMINATED WITH HEAVY METALS

WPŁYW MATERII ORGANICZNEJ Z RÓŻNYCH ŹRÓDEŁ NA PLON I JAKOŚĆ ROŚLIN NA GLEBACH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

Abstract: Continuous civilization progress, growing level of industrialization, and urbanization cause that the contents of heavy metals in the environment is increasing with a risk of biota and groundwater contamination. The experiment was carried out in stoneware pots sank into the ground filled up with 56.4 kg of soil: Haplic Luvisols formed from loamy sand. The soil was mixed up with liquid form of salts: $Cd(NO_3)_2$, $Pb(CH_3COO)_2$ and $ZnSO_4$. To the soil a brown coal preparation, so called "Rekulter", brown coal, peat and farmyard manure were applied in the amount of 180, 140, 390 and 630 g per pot, which is equivalent to 5 Mg of organic carbon per ha. Winter rye (*Secale cereale)* was harvested in green forage. The manurial value of organic substance originated from different sources expressed as the plants' crop was the highest for Rekulter and the lowest for peat. The addition of organic substance to soil contaminated with heavy metals causes the higher content of phosphorus in rye's roots. The content of sodium in the rye's above - grounds parts did not depend from addition of organic matter to soil. The contents of nitrogen in rye on contaminated soil were higher in comparison with plants from soil without heavy metals.

Keywords: organic matter, yield, soil contaminated with heavy metals, macroelements

Due to various anthropogenic activities, potentially toxic metals are accumulated in soils, with a risk of biota and groundwater contamination. Among the various reactive soil constituents soil organic matter has a large sorption capacity towards metal ions [1, 2]. Organic matter has been considered to preserve a record amount of heavy metals. The protective role of organic matter towards plants lies in forming simple and chelate complex compounds with ions of heavy metals. Maintenance of adequate organic matter levels in the soils is also very important to maintain soil fertility and sustainable crop production.

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In Poland, soils species (predominantly sandy soils) and inadequate land management have led to a reduction in the organic matter content of soils. This effect is intensified by the limited availability and high cost of manure and the popular use of mineral fertilizers. Therefore, new sources of organic matter have been tapped, such as municipal solid waste compost, low energetic value brown coal and sewage sludge [3, 4]. Moreover, the produced low-cost brown coal preparation could be used as amendment in agriculture, meanwhile recycling its valuable components: organic matter, N, P, K and other plant nutrients [5]. Application of the no-conventional sources of organic matter to agricultural soils was found to improve micronutrient complex formation, which increases availability of micronutrients to plants, to stimulate the presence of beneficial soil organisms and to reduce the presence of plant pathogens. Moreover, it seems to increase water holding capacity, soil buffering and cation exchange capacity and it improves soil porosity [6, 7]. Application of brown coal preparations as a source of organic matter is a practice to improve soil properties [8].

The aim of the present work was to determine the effect of organic matter from different sources (brown coal preparation, so-called "Rekulter", brown coal, peat and farmyard manure) on yield and plant (*Secale cereale* L.) quality (content of macroelements: K, Mg, Ca, Na, P and N) cultivated on heavy metals contaminated soils.

Materials and methods

The experiment was carried out in stoneware pots of a diameter of 40 cm and a height of 120 cm sank into the ground filled up with 56.4 kg of soil: Haplic Luvisols originated from loamy sand, situated in an open area. To the soil a brown coal preparation, so-called "Rekulter", brown coal, peat, and farmyard manure were applied in the amount of 180, 140, 390, and 630 g per pot, which is equivalent to 5 Mg of organic carbon per ha. The Rekulter contained 85% brown coal, 10% peat, 4% brown coal ash, and 1% mineral fertilizers. The soil was mixed up with liquid form of salts: cadmium as $Cd(NO_3)_2$, lead as $Pb(CH_3COO)_2$ and zinc as $ZnSO_4$, which after blending led to the following concentrations of heavy metals (in $mg \cdot kg^{-1}$ of soil): 90.0 (Zn), 60.4 (Pb) and 0.80 (Cd).

Soil samples were taken at the depth of 20 cm, in the first year after the application of amendments. In the soil samples the following data were determined: pH_{H20} and pH_{KCl}, *total organic carbon* (TOC) content by Tiurin's method, *total nitrogen* (Nt) content by Kjeldahl's method.

Winter rye (*Secale cereale*) was harvested in green forage. Plants were collected and washed, weighted, and dried at 60°C to constant weight. Content of macroelements: K, Mg, Ca, Na, P in plant samples were determined by atomic absorption. Nitrogen after mineralization in concentrated H_2SO_4 by Kjeldahl's method.

Results and discussion

From the experiment it follows that introduction into the soil of organic matter coming from various sources changes physicochemical properties of the soil (Table 1). The highest increase in pH ($pH_{H2O} = 5.35$; $pH_{KCl} = 4.98$) was found in the stonepots (soil without heavy metals), where the Rekulter was used, and the smallest increase occurred in objects (soil without heavy metals) with manure ($pH_{H2O} = 4.95$; $pH_{KCl} = 4.51$).

In objects with brown coal (soil contaminated or not contaminated with heavy metals), the *total organic carbon* (TOC) amounted to about 12 $g \cdot kg^{-1}$; in the stonepots with the

Rekulter to about 15 g·kg^{-1}, while in the objects with peat or farmyard manure it was about 8 g·kg^{-1}. The highest growth in the *total nitrogen content* (0.658 g·kg^{-1}) occurred with the Rekulter, and the lowest (0.502 g·kg^{-1}) in the object with peat. The widest range of TOC to Nt ratio came about with the Rekulter, which was due to the highest TOC content in this object. Other authors experimenting with Rekulter and brown coal obtained similar results [7, 8].

Table 1

The basis properties of soil samples

Objects	**pH in**		**TOC**	**Nt**	**TOC:Nt**
	H_2O	**KCl**	**[g·kg^{-1}]**		
Control	4.93	4.38	7.35	0.465	15.8
Control + heavy metals	4.95	4.33	7.93	0.473	16.7
Rekulter	5.35	4.98	15.01	0.626	23.9
Rekulter + heavy metals	5.30	4.97	15.40	0.658	23.4
Peat	5.25	4.69	8.07	0.502	16.1
Peat + heavy metals	5.05	4.72	8.10	0.504	16.0
Farmyard manure	4.95	4.51	8.25	0.532	15.5
Farmyard manure + heavy metals	4.98	4.55	8.55	0.538	15.9
Brown coal	5.20	4.92	12.30	0.598	20.6
Brown coal + heavy metals	5.15	4.93	12.65	0.594	21.3
LSD α = 0.05	0.021	0.024	0.17	0.025	0.47

Notation: LSD - least significant difference, TOC - total organic carbon, Nt - total nitrogen

Due to high phytotoxicity of heavy metals especially cadmium, the effect of this element on the growth, yielding and quality characters of crops has been investigated in numerous experiments. Soil contamination with cadmium tends to have an adverse influence on the yield of plants. Ghani [9] proved that cadmium decreased general yield of mungbean. Ciecko et al [10] showed that cadmium soil pollution caused a much greater decline of green matter yield in maize than in oats. Organic amendments eg farmyard manure, peat contain plant nutrients and organic matter, which are beneficial to soils with respect to their productivity as well as for reclamation purposes.

Table 2

The yield of aboveground part of rye of fresh and dry mass [g · pot^{-1}]

Objects	***Fresh mass***	***Dry mass***
Control	386.3	126.5
Control + heavy metals	306.3	96.3
Rekulter	641.6	207.6
Rekulter + heavy metals	453.8	155.5
Peat	447.2	151.2
Peat + heavy metals	310.5	82.3
Farmyard manure	615.2	191.5
Farmyard manure + heavy metals	360.0	125.3
Brown coal	548.8	166.5
Brown coal + heavy metals	361.8	114.3
LSD α = 0.05	39.81	30.71

It comes out from the experiment, that introduction of organic matter from different sources, into heavy metals' contaminated soil influenced, on yield and plant quality (Tables

2-4). The manurial value of organic substance originated from different sources expressed as the plants' crop was the highest for Rekulter and the lowest for peat. In the present trial contamination of soil with cadmium, lead and zinc caused a high decline in the yield of above - ground part of rye of fresh and dry mass reaching, respectively, 79 and 76% compared with objects without heavy metals (Table 2). By adding the Rekulter, brown coal, peat and farmyard manure, the negative influence of heavy metals on yield of rye was neutralised. The highest yield of rye of fresh and dry mass was in case were Rekulter was applied. It acts by creating better soil conditions for plants' vegetation. Similar results were reported by Ciecko et al [11], they found out that addition of brown coal into contaminated soil caused a considerable increase in the yield of aboveground part of triticale.

Calcium. Tables 3, 4 and 5 show the changes in plant composition, due to the heavy metals and different sources of organic matter treatment, in terms of the ratio of the concentration of Ca, Mg, K, Na, N or P in plants grown. The addition of organic substance to soil causes the higher content of calcium in roots, stalk and ear (Table 3). The increase of content of calcium in rye was higher in objects without heavy metals. High concentrations of heavy metals, especially Zn^{2+} ions may cause limited sorption of calcium ions, what directly diminishes the cementing of cell walls by calcium pectinates that leads to the maceration of root tissue [12, 13]. In all examined parts of rye contents of calcium was the highest on object with Rekulter. Contents of calcium were the smallest in ear.

Magnesium. Contents of magnesium in rye increased, after addition of organic matter from different sources in comparison with control object (Table 3). In all examined parts of rye contents of magnesium was the highest on object with Rekulter. Just as in case of calcium, there was in ear the smallest contents of magnesium, which was apparently translocated from roots to aboveground part of rye. Stalk magnesium concentrations in this study ranged from 0.95 to 1.19 g·kg^{-1} compared with 2.40÷3.12 g·kg^{-1} in a companion field study [14].

Table 3

Calcium, magnesium and potassium content in rye dry mass [g·kg^{-1} d.m.]

Objects	**Roots**			**Stalk**			**Ear**		
	Ca	**Mg**	**K**	**Ca**	**Mg**	**K**	**Ca**	**Mg**	**K**
Control	2.78	0.82	15.5	1.78	0.95	10.5	1.50	0.56	17.6
Control + heavy metals	1.78	0.74	12.5	0.82	1.18	14.0	0.60	0.87	27.5
Rekulter	2.89	0.94	13.2	2.64	1.12	11.5	2.35	0.69	17.4
Rekulter + heavy metals	1.90	0.79	10.3	0.94	1.19	12.6	0.76	0.89	23.5
Peat	2.87	0.87	13.5	1.94	0.99	11.6	1.60	0.57	16.5
Peat + heavy metals	1.80	0.80	13.8	0.85	1.16	13.2	0.75	0.88	22.5
Farmyard manure	2.80	0.85	11.0	2.43	1.00	12.1	1.95	0.56	18.4
Farmyard manure + heavy metals	1.85	0.78	10.8	0.86	1.09	13.0	0.67	0.87	23.7
Brown coal	2.83	0.89	12.5	2.59	0.99	11.6	2.30	0.67	17.7
Brown coal + heavy metals	1.87	0.82	11.2	0.89	1.12	12.0	0.69	0.88	21.7
LSD$_{0.05}$	0.31	0.05	1.10	0.09	0.02	2.02	0.19	0.18	3.38

Potassium. Whitehead [15, 16] reported potassium concentration of 25 g·kg^{-1} as typical of grass, with different species in the range of 15÷35 g·kg^{-1} (ryegrass and white clover). Rye from this experiment had potassium concentrations range from 10 to 27 g·kg^{-1} (Table 3). Contents of potassium in roots of rye, significantly decreased, influenced by addition of organic matter in comparison with control object. However, contamination of soil with heavy metals, significantly increase potassium uptake by plants. The study suggested that rye is relatively tolerant to heavy metal concentrations. The accumulation of potassium in roots was smaller than in aboveground part of rye.

Sodium. Content of sodium in roots was the smallest in variant with Rekulter whereas the highest in variant with farmyard manure on both contaminated soil and without heavy metals (Table 4). Content of sodium was the biggest in stalk in control variant and with farmyard manure. Organic matter from different sources did not effect on content of sodium in ears in variants on soil contaminated or without heavy metals.

Phosphorus. Addition of organic matter from different sources into soil has not caused growth of content of phosphorus in roots (Table 4). Content of phosphorus in biomass of rye has grown influenced by added organic matter on soil contaminated with heavy metals. It was also observed that the highest content of this macronutrient was in stalk, in all variants. Contents of phosphorus in ear did not differ significantly depending on source of organic matter added into soil relatively to control. The results confirm researches of other authors [17] where addition of brown coals' ash caused decrease of contents of phosphorus in plants.

Nitrogen. It was observed the smallest content of nitrogen in roots in object with peat from uncontaminated soil whereas, the highest in variants with the Rekulter and brown coal (Table 4). Content of nitrogen in biomass of rye was significantly higher on soil contaminated in comparison with soil without heavy metals. Added into soil organic matter did not influence on growth of content of nitrogen in stalk and ear. It catches on generally, that mineral fertilization supported by organic fertilization it plays decisive effect on in forming of harvest of plant and their chemical compositions [17, 18]. The results obtained from this research confirmed them.

Table 4

Sodium, phosphorus and nitrogen content in rye dry mass [g·kg^{-1} d.m.]

Objects	**Roots**			**Stalk**			**Ear**		
	Na	**P**	**N**	**Na**	**P**	**N**	**Na**	**P**	**N**
Control	0.27	2.03	50.3	0.25	2.43	68.9	0.20	1.50	86.9
Control + heavy metals	0.22	1.33	112	0.26	2.93	130	0.21	1.89	122
Rekulter	0.23	1.54	56.6	0.22	2.47	48.8	0.20	1.51	82.8
Rekulter + heavy metals	0.21	2.20	65.1	0.21	2.76	137	0.20	1.60	176
Peat	0.25	1.77	36.5	0.22	2.54	48.9	0.20	1.60	79.2
Peat + heavy metals	0.23	1.91	55.6	0.21	2.62	136	0.20	1.80	195
Farmyard manure	0.27	1.55	49.8	0.25	2.76	55.1	0.20	1.48	80.9
Farmyard manure + heavy metals	0.33	1.79	86.4	0.25	2.66	140	0.20	1.80	199
Brown coal	0.25	1.85	54.6	0.22	2.59	52.1	0.20	1.71	78.3
Brown coal + heavy metals	0.26	1.98	59.0	0.24	2.67	139	0.20	1.79	188
$LSD_{0.05}$	0.02	0.04	5.1	0.01	0.06	7.0	0.01	0.08	8.6

The ratio of potassium to sum of calcium and magnesium could be used to express the relationships between K content and Ca plus Mg contents, respectively [19]. The ratio of potassium to sum of calcium and magnesium decide about forage usefulness of plant. It catches on, that this ratio should not be widest in plants than 2.5 : 1, so, danger gets in case of all objects (Table 5). Under influence of organic matter from different sources the contents of calcium and magnesium in rye increased and reduced the ratio K : (Ca + Mg) in plants which influenced on theirs fodder quality.

Table 5

Ratio K : (Ca + Mg) in rye

Objects	Stalk	Ear
Control	3.84	8.54
Control + heavy metals	6.99	18.40
Rekulter	3.05	5.71
Rekulter + heavy metals	5.91	14.22
Peat	3.95	7.60
Peat + heavy metals	6.56	13.77
Farmyard manure	3.52	7.33
Farmyard manure + heavy metals	6.66	15.38
Brown coal	3.24	5.95
Brown coal + heavy metals	5.97	13.82

Conclusions

Organic matter originated from different sources application into soil increased soil pH, content of total organic carbon (TOC) and total nitrogen. In variant with the Rekulter, this led to significant increases of yield and its quality compared with farmyard manure, peat and brown coal treatments. The addition of organic substance into soil contaminated with heavy metals causes the higher content of phosphorus in rye's roots. The content of sodium in the rye's above the grounds parts did not depend from addition of organic matter into soil. Plants cultivated on contaminated soil contained more nitrogen in comparison with soil without heavy metals.

Basing on the final results it can be stated that the Rekulter had the biggest, positive influence on analysed factors compared with farmyard manure, peat and brown coal. Under the influence of the Rekulter the contents of calcium and magnesium in rye increased and reduced the ratio K : (Ca + Mg) in plants which influenced on their fodder quality.

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WPŁYW MATERII ORGANICZNEJ Z RÓŻNYCH ŹRÓDEŁ NA PLON I JAKOŚĆ ROŚLIN NA GLEBACH ZANIECZYSZCZONYCH METALAMI CIĘŻKIMI

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Abstrakt: Badania prowadzono w wazonach kamionkowych umieszczonych w gruncie, które wypełniono glebą płową właściwą (wg WRB. Haplic Luvisols) wytworzoną z piasku gliniastego lekkiego na glinie lekkiej. Do gleby wprowadzono metale ciężkie w formie soli: $ZnSO_4$, $Pb(NO_3)_2$ i $Cd(NO_3)$. Jednocześnie do gleby dodano jednorazowo: nawozu organiczno-mineralnego z węgla brunatnego „Rekulter”, węgla brunatnego, torfu lub obornika w dawkach odpowiednio 180, 140, 390, lub 630 g na wazon, co odpowiadało 5 Mg C_{org} na ha. W doświadczeniu uprawiano żyto ozime na zieloną masę. W próbkach roślinnych oznaczono ogólną zawartość wapnia, magnezu, sodu, potasu, fosforu i azotu. Celem badań było określenie wpływu dodatku materii organicznej z różnych źródeł do gleby zanieczyszczonej metalami ciężkimi na plonowanie żyta oraz zawartość i rozmieszczenie K, Na, Mg, Ca, P i N w życie. Wartość nawozowa substancji organicznej z różnych źródeł wyrażona plonem roślin była największa dla Rekultera, a najmniejsza dla torfu. Dodatek substancji organicznej do gleby powoduje wzrost zawartości K, Mg, P i N w źdźble i kłosie żyta. Zawartość sodu w nadziemnych częściach żyta nie zależała od zanieczyszczenia gleby metalami ciężkimi i dodatku materii organicznej. Zawartość azotu w życie na glebie zanieczyszczonej była wyższa w porównaniu do roślin z gleby bez metali ciężkich.

Słowa kluczowe: materia organiczna, gleba zanieczyszczona metalami ciężkimi, plon, makroelementy

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TRANSFER OF CESIUM-137 FROM FOREST SOIL TO MOSS *Pleurozium schreberi*

TRANSFER CEZU-137 Z GLEBY LEŚNEJ DO MCHU *Pleurozium schreberi*

Abstract: Moss (*Pleurozium schreberi*) and soil samples collected in 2009 in Bory Stobrawskie forest were used to study the transfer factor (TF_{Cs}) and aggregated transfer factor (Tag) of radiocesium from forest soil to moss. This investigation also included determination of ^{40}K activity, pH, conductivity and organic matter content in soil. The mean ^{137}Cs activities were 179 Bq/kg d.m. in soil samples and 203 Bq/kg d.m. in moss. The TF_{Cs} of ^{137}Cs from soil to moss was varied in the range from 0.1 to 3.3. The mean surface activity was 11.2 kBq/m^2. The Tag values were limited in the range from 0.001 to 0.058. Additionally the TF_K values for ^{40}K were computed. It was found that the main contribution of ^{137}Cs activity in environment originates from soil and activities of ^{137}Cs and ^{40}K were usually higher in moss than in soil. It can be supposed that the ^{137}Cs isotope migrates to moss from its surrounding. Among others, statistically significant correlation between TF of ^{137}Cs and activity of ^{40}K in soil was found. Low activity of ^{40}K in soil is conducive to the transfer of cesium to moss. The organic matter content also affects transport of cesium and potassium between moss and soil.

Keywords: transfer factor, moss, radioactivity, ^{137}Cs, ^{40}K

Since 1986, after the breakdown in Chernobyl nuclear power plant, intensification of radioecological research has emerged. In the scientific literature many papers on behaviour of ^{137}Cs in soil and migration in vegetation [1-4] have been published. In studies conducted in Venezuela, the transfer coefficient (TF) of ^{137}Cs from soil to moss was estimated. TF in the Altos area were 2.60÷2.91, while in the La Sierra they were only 0.59÷0.77 [5]. The concentration of cesium in moss and soil was correlated with the height at which samples were taken. Other studies [6] showed that accumulation of ^{137}Cs in mosses is correlated with the concentration of this radionuclide in the atmospheric precipitation. The transfer coefficient of ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs in mosses was also studied by Dragović [7]. The relationship between concentration ratios of radionuclides and physicochemical

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characteristics of the underlying soil was also investigated. Generally the highest activity concentrations were found to be in *Hypnum cupressiforme* and the lowest ones in *Hylocomium splendens*.

Uptake of radionuclides by vegetation at a High Arctic location was also studied [8]. Levels of ^{137}Cs activities in vegetation generally followed the order moss > lichen > vascular plants. The uptake of ^{137}Cs in vascular plants showed an inverse relationship with the uptake of ^{40}K. The uptake of ^{238}U, ^{226}Ra and ^{232}Th by vascular and non-vascular plants was generally low. Uptake of ^{137}Cs and ^{40}K by plants was also studied by Korobova [9]. The concentrations determined in samples of plants corresponded to the regional values and varied in the range from 31 to 140 Bq/kg d.m. Activities increased in the main plant groups according to their phylogenetic specificity in the following order: grasses < alder, willow (leaves) lichen < moss (upper part) < moss (lower part, litter). Moss and their lower brownish part in particular, appeared to be most enriched in ^{137}Cs, while lichen, associated with moss but receiving contaminants exclusively through air precipitation, accumulated radionuclides to a lesser extent.

In this work we have used moss *Pleurozium schreberi* to study *transfer factor* (TF) and *aggregated transfer factor* (Tag) of radiocesium from forest soil to plant.

Materials and methods

Samples of the moss *Pleurozium schreberi* and soil were collected in forests around Opole (south-western Poland) in autumn 2009. The samples were dried at room temperature. The material investigated was composed of both green and brown parts of a moss. Any impurities were removed manually from material. From the bared moss bed the samples of soil layer of 10 cm thick were taken. The sampling sites were located in Bory Stobrawskie forest, in the northeast direction from Opole. The places were situated not less than 200 m from roads, close to Lubsza, Makoszyce, Siolkowice, Pokoj, Zagwizdzie, Masow, Kotorz, Kadlub, Krasiejow, Laziska, Kolonowskie, Jemielnica, Zedowice, Kosorowice, Klekotna, Knieja, Olesno, Szumirad, Bazany and Os. This region is rather flat, without significant irregularities in its elevation.

The measurement of ^{137}Cs and ^{40}K activity in moss (a_m) and soil samples (a_s) 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 the standard solutions type MBSS 2 (Czech Metrological Institute, Prague, CZ) which covers an energy range from 59.54 keV 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. The measurement uncertainties were different for different materials. The measurement error of ^{137}Cs activity in soil was about 5% and about 10% for ^{40}K activities. Measurement errors of moss activity were bigger, the average value for ^{137}Cs was 10% and 30% for ^{40}K.

The ^{137}Cs surface activities (aCs_a) were measured with Canberra portable scintillation spectrometer InSpector1000. This spectrometer is an easy-to-use, hand-held, digital and multichannel analyzer ideal for the environment monitoring purposes. The average error of surface activity measurements was about 7%.

The following physicochemical properties of soil were determined, using methods generally applied in soil science [10, 11]:

- soil acidity - by the potentiometric method in distilled water (pH);
- organic matter content (OM);
- electrical conductivity (σ).

Values of the following parameters were measured: ^{137}Cs and ^{40}K activities in moss (aCs_m and aK_m, respectively), ^{137}Cs and ^{40}K activity in 10 cm top soil layer (aCs_s and aK_s, respectively), ^{137}Cs surface activity (aCs_a).

From aCs_m, aCs_s and aCs_a the transfer factor (TF) and aggregated transfer factor values (Tag) were computed.

The TF and Tag values are commonly used for quantifying radionuclides uptake by plant. Dimensionless TF values can be conveniently defined as the ratio of the activity concentrations of plant material a_m and the soil a_s on which the plant has grown expressed in Bq/kg of dry mass:

$$TF = a_m/a_s \tag{1}$$

The Tag values are calculated as the ratio of the radionuclide activity concentration in dry mass of an organism to the surface activity (a_a) of the nuclide [8]:

$$Tag = a_m/a_a \tag{2}$$

For statistical computations, the R language was utilized [12]. R is a free software environment for statistical computing and its functions can be extended by additional libraries. For our computation the functions provided by the "MASS" [13], "StatDA" [14], "car" [15] and "nortest" [16] libraries of R were used. Normality of variables distributions was tested using Anderson-Darling, Cramer-von Mises, Lilliefors (Kolmogorov-Smirnov), and Shapiro-Francia tests. For linear regression computations the standard and robust methods were utilized. The robust method was based on MM-estimation.

Results and discussion

Table 1 shows the main statistical parameters of the results obtained. In this Table min. is the lowest value in data, Q_l is lower quartile, ME is median, Q_u is upper quartile, max. is the highest value, x_m is arithmetic mean, SD is standard deviation, and MAD is median absolute deviation, respectively. To asses the parameters variability the coefficient of variation CV and the ratio of MAD and median were calculated.

In most of the moss samples both ^{137}Cs and ^{40}K activities were higher in moss than in soil. The transfer factors of Cs and K were similar, supposing common mechanism of this elements transfer from soil to moss. Considerable differences between mean value and median of some parameters, eg ^{137}Cs activities in soil and in moss, suppose highly skewed distribution of variables or existence of outliers in data. Comparison of dispersion measures CV and more robust MAD/ME ratio also indicates outliers existence in data, particularly for aK_m.

It was found that distributions of our data were different from each other. This may cause problems in interpretation of significance test results and in covariability studies. To diminish influence of this feature on inference reliability the variables were transformed to make their distributions similar to the normal one. Besides the OM values expressed in wt. % the other variables were transformed using the Box-Cox formulas. If the original random variable is x and the transformed one is x′, the Box-Cox formula can be expressed by the following relationships (Eqs 3a-b):

$$x' = (x^w - 1)/w \quad \text{for } w \neq 0 \tag{3a}$$

$$x' = \log(x) \quad \text{for } w = 0 \tag{3b}$$

where w is the dimensionless exponent.

Table 1

Statistical parameters of the measurements results and values of computed parameters

	aCs_m [Bq/ kg d.m.]	**aCs_s [Bq/ kg d.m.]**	**TF_{Cs} [-]**	**aK_m [Bq/ kg d.m.]**	**aK_s [Bq/ kg d.m.]**	**TF_K [-]**	**aCs_a [kBq/ m^2]**	**Tag [m^2/kg]**	**OM [%]**	**pH [-]**	**σ [mS/ cm]**
min.	20	9	0.11	124	108	0.87	0.36	0.001	4.39	3.52	36.9
Q_l	41	29	0.77	177	136	1.02	1.74	0.016	9.5	3.86	65.1
ME	63	50	1.44	224	161	1.39	6.21	0.021	17.25	3.99	86.8
x_m	203	179	1.43	285	160	1.83	11.17	0.023	20.57	4.17	97.9
Q_u	252	277	1.77	281	178	1.89	13.7	0.031	26.64	4.26	115.1
max.	1234	696	3.28	1530	226	9.25	41.6	0.058	53.27	5.43	290.4
SD	287	208	0.74	292	35	1.78	13.41	0.013	15.25	0.50	53.1
MAD	62	55	0.65	71	34	0.61	7.29	0.013	11.86	0.25	35.8
CV	1.4	1.2	0.52	1.0	0.22	0.97	1.2	0.57	0.74	0.12	0.54
MAD/ ME	1.0	1.1	0.45	0.3	0.21	0.44	1.2	0.64	0.69	0.06	0.41

The exponents found for each column of data frame were utilized for x′ computations. The w exponent values are shown in Table 2.

Table 2

Values of the w exponent calculated for variables

Parameter	**aCs_m**	**aCs_s**	**TF_{Cs}**	**aK_m**	**aK_s**	**TF_K**	**aCs_a**	**Tag**	**pH**	**σ**
w	–0.247	–0.053	0.712	–1.11	0.016	–1.11	0.011	0.631	–4.64	–0.234

Values of the OM variable were transformed using the logit transformation.

Several functions from package "nortest" were used to test normality of transformed variables distributions. The p-values computed for all of the transformed variables were considerably higher than the 0.05 limit, usually accepted in statistical testing. Presumption of normal distributions of the transformed data should not be rejected.

In statistical analysis the possibility of outliers existence in data was taken into account. To observe influence of outliers on results of covariability examination function "CorCompare" from "StatDA" R package were used. The correlation matrixes were calculated using standard and the robust *minimum covariance determinant* (MCD) methods. Figure 1 shows a square matrix in which the cells below diagonal contain values of correlation coefficients r computed in standard way (r_s, upper number) and using MCD (r_{MCD}, lower number). Above diagonal ellipses are drawn, which axes aspect ratio reflects values of correlation coefficient.

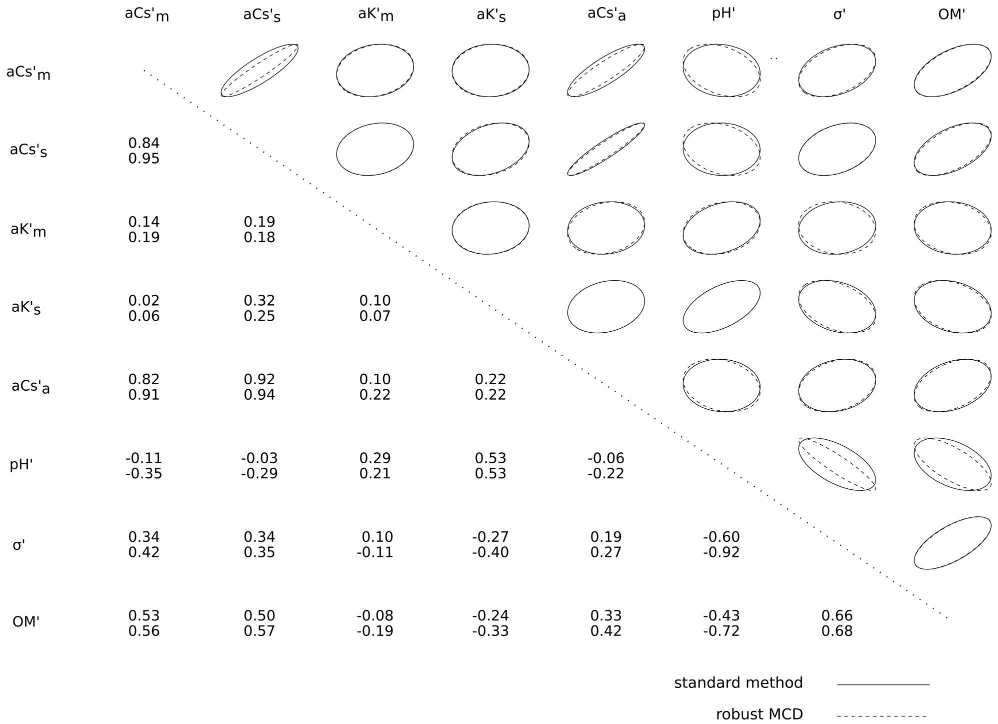

Fig. 1. Values of correlation coefficients computed with standard and MCD methods, and their graphical representation

Bigger absolute r_{MCD} values than r_s can be observed for some of variables pairs. Though most of differences between correlation coefficients are not big, for further computations the correlation coefficients computed with the robust MCD method were taken.

The best correlations were observed between pairs of variables representing ^{137}Cs activities in soil, in moss and its total surface activity. Also organic matter content OM is well correlated with ^{137}Cs activities in moss and in soil. Activity of ^{40}K in soil is well correlated with pH of 10 cm soil layer.

Table 3 shows results of eigenvalues decomposition of correlations matrix. In this table the principal components loadings PC1 to PC8 and their components are shown. The s^2 is the variance of the principal components scores, s_r^2 is the ratio (proportion) of the PC's variance and sum of all variances, s_c^2 is the cumulative proportion of PC's variance.

The first five components contain about 93% of the total data variability. But only first three of them contain significant variances and should be considered in evaluation of mutual relationships in data. In the first PC containing 39% of variance nearly all of variables are well represented. Contribution of the ^{40}K activities in PC1 is very poor. The investigated area was contaminated by ^{137}Cs unevenly. Its activity in components of forest environment is much more spatially differentiated than the one of naturally occurring ^{40}K isotope. Regions of significantly lower or higher than the mean ^{137}Cs activities can be distinguished in the area investigated, whereas distribution of potassium is relatively homogenous. Interrelations between soil parameters might be result of the presence of organic matter decay products. Acidic compounds decrease pH of solution and, as a result of high hydrogen cation mobility, increase in electrical conductivity is observed. The main components of PC2 are ^{40}K activity in soil, surface ^{137}Cs activity and pH. Since ^{40}K is naturally occurring isotope with constant ratio to stable potassium isotopes (^{39}K and ^{41}K), its activity is a measure of total potassium concentration in a sample. Surface ^{137}Cs activity is a measure of total amount of this isotope in environment. The main contribution to surface activity is supplied by soil but contribution of environment components is also significant. The variables contributing PC2 suppose an influence of pH and potassium content in soil on cesium transfer to moss. The PC3 component supposes an interrelation between potassium concentrations in soil and in moss, though it is rather weak.

Table 3

Results of eigenvalues decomposition and statistical parameters of PCs ordered by decreasing variances of scores

	PC1	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**	**PC7**	**PC8**
aCs_m	–0.45	–0.26	0.02	–0.21	0.20	–0.56	0.36	–0.45
aCs_s	–0.43	–0.33	–0.09	–0.07	–0.04	–0.05	0.15	0.81
aK_m	–0.02	–0.31	0.88	0.23	–0.26	0.06	0.04	–0.04
aK_s	0.09	–0.50	–0.43	0.68	–0.23	0.04	0.11	–0.18
aCs_a	–0.40	–0.37	–0.03	–0.16	0.31	0.56	–0.46	–0.24
pH	0.36	–0.42	–0.05	–0.31	–0.16	–0.47	–0.59	0.06
σ	–0.38	0.34	0.08	0.54	0.19	–0.37	–0.51	0.07
OM	–0.42	0.21	–0.13	–0.18	–0.82	0.05	–0.13	–0.18
s^2	0.86	0.61	0.31	0.16	0.11	0.08	0.06	0.02
s_r^2	39	28	14	7	5	3	3	1
s_r^2	39	67	81	88	93	96	99	100

Contribution in variation of the remaining components is much smaller than the three first of them.

To examine relationships between transfer factors of elements and physicochemical properties of soil the linear regression method was utilized. To avoid improper computational data interpretation both standard and robust methods were used. It was found that ^{137}Cs moss/soil transfer factor (TF_{Cs}) was interrelated with potassium content in soil. The correlation coefficient was –0.63 (p-value = 0.002). Detailed analysis of the relationship between transformed TF_{Cs} and aK_s supposed a good linearity and no influential points. It can be supposed that potassium reduces cesium transfer to moss in a competitive process. The Tag parameter is also related to aK_s, though outlying points conceal this relationship. In Table 4 the parameters of the linear relationships with slope m and intercept b, computed both with standard and robust methods are shown. Additionally the standard errors *SD* of m and b are presented.

Influence of potassium content in soil and its physicochemical properties on ^{137}Cs transfer factors was observed. Though mosses have only a rudimentary root system and readily take up elements from the atmosphere, some processes affecting element uptake were supposed. Among them transport of soluble compounds from the soil into the moss tissue during periods with extensive soil/water contact, ion exchange of metal with sea-salt cations and H^+ from acidic precipitation, and internal redistribution of elements within the moss plant were mentioned [17, 18]. Potassium from soil dust partly dissolved in atmospheric water may change ion concentrations enough to affect cesium uptake by moss. Composition of soil dust may locally determine properties of water precipitate, changing its pH or ionic strength. This phenomenon may affect not only cesium uptake but also uptake of other elements.

Table 4

Parameters of the linear relationships with slope m and intercept b, computed both with standard and robust methods

		m	**SE_m**	**b**	**SE_b**
TF_{Cs}	standard	–1.86	0.53	10.1	2.8
	robust	–1.83	0.56	10.0	3.0
Tag	standard	–0.091	0.049	–0.96	0.26
	robust	–0.123	0.049	–0.80	0.16

Conclusions

The main contribution of ^{137}Cs activity in environment originates from soil. Concentration of both ^{137}Cs and ^{40}K was usually higher in moss than in soil. It can be supposed that the ^{137}Cs isotope migrates to moss from its surrounding. Low activity of ^{40}K in soil conducive to the transfer of cesium to moss. The organic matter content also affects transport of cesium between moss and soil.

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TRANSFER CEZU-137 Z GLEBY LEŚNEJ DO MCHU *Pleurozium schreberi*

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Abstrakt: Mech (*Pleurozium schreberi*) i próbki gleby pobranej w 2009 roku w Borach Stobrawskich wykorzystywano do badania współczynnika transferu (TF_{Cs}) i zbiorczego współczynnika transferu (Tag) radiocezu z gleb leśnych do mchu. Określono także aktywność ^{40}K, pH, konduktywność i zawartość materii organicznej w próbkach gleby. Średnia aktywność ^{137}Cs wynosiła 179 Bq/kg s.m. w próbkach gleby i 203 Bq/kg s.m. w próbkach mchu. Współczynnik transferu TF_{Cs} z gleby do mchu zmieniał się w zakresie od 0,1 do 3,3. Średnia aktywność powierzchniowa wynosiła 11,2 kBq/m^2. Wartości Tag mieściły się w zakresie od 0,001 do 0,058. Zostały także obliczone wartości TF_K dla ^{40}K. Stwierdzono, że główny udział aktywności ^{137}Cs w środowisku pochodzi z gleby, a aktywności ^{137}Cs i ^{40}K były zwykle większe w mchu niż w glebie. Znaleziono istotną statystycznie korelację pomiędzy TF_{Cs} i aktywnością ^{40}K w glebie. Sugeruje to, że mała zawartość potasu w glebie sprzyja przenoszeniu cezu do mchu. Zawartości materii organicznej również wpływają na transport cezu i potasu pomiędzy mchem i glebą.

Słowa kluczowe: współczynnik transferu, mech, radioaktywność, ^{137}Cs, ^{40}K

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PHOTODEGRADATION OF *n*-BUTYLPARABEN IN NATURAL WATER FROM SULEJOW RESERVOIR

FOTODEGRADACJA KSENOBIOTYKU *n*-BUTYLOPARABENU W WODZIE Z ZALEWU SULEJOWSKIEGO

Abstract: Removal of *n*-butylparaben (BP) - a compound which disrupts the endocrine system - from pure water and natural water taken from Sulejow Reservoir was investigated. Target compound degradation was performed using photochemical methods: direct photolysis by UVC irradiation, advanced oxidation in an H_2O_2/UV system and photosensitized oxidation employing a xenon arc lamp as a solar radiation simulator with two sensitizers. In the course of direct photolysis by UVC light (λ = 254 nm) and degradation in the H_2O_2/UV system, no or slight influence of the natural water matrix was observed, respectively. In the case of photosensitized oxidation, the decrease of BP concentration was 15% higher in natural water in comparison to pure water.

Keywords: EDCs, *n*-butylparaben, natural water, H_2O_2/UV system, photosensitized oxidation

The Sulejow Reservoir, from which natural water sample was taken, is a shallow (average depth: 3.3 m), lowland dam reservoir, covering 23 km^2 at full capacity. The reservoir is an important freshwater resource for the city of Lodz [1]. As with most artificial reservoirs, Sulejow Reservoir faces several problems like cyanobacterial blooms, which results in water quality deterioration [2]. To assure proper functioning of the water ecosystem and effective use of the natural potential for self-purification, maintenance of its homeostasis is crucial. The presence of *endocrine disrupting compounds* (EDCs) in industrial effluents and, as a result, in freshwater and drinking water supplies, poses serious environmental concern. Among others, EDCs are responsible for male fish feminization, disruption of sex structure of a population, reduced sperm counts, hermaphroditism, changes in nuptial behavior and vertebrate infertility [3, 4]. An exposure to EDCs affects not only at the individual organism scale, but can influence whole populations. It can lead to a domino effect, causing changes in the trophic network and disturbing the normal functioning of the ecosystem.

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Butylparaben (BP) is a substance widely used as a preservative, mainly in cosmetics, and has been regarded as harmless for a long time. However, a number of reports confirming BP estrogenic activity is rising [5-7]. EDCs can cause harmful effects on wildlife even at very low concentrations [8]. Yamamoto et al [9] reported that the maximum no-effect concentration determined by male medaka VTG assay for *n*-butylparaben was 40 μg dm^{-3} ($2\cdot10^{-7}$ mol dm^{-3}) and the predicted no-effect concentration determined on the basis of conventional acute/chronic tests was 8.0 μg dm^{-3}. Therefore, there is a need for an effective method for BP removal from water to be found.

In natural water bodies BP undergo slow biodegradation with half-live times ranging from 9.5 to 16 h (temperature range 20÷28°C) [10]. The chlorination of *n*-butylparaben solution by addition of 2.0 mg dm^{-3} chlorine as sodium hypochlorite (NaClO) for 15 min caused a decrease in BP initial concentration (C_0 = $5.15\cdot10^{-7}$ M) by 67% [9]. Still, the formation of halogenated by products of parabens in chlorinated water was found [11]. The batch sunlight photolysis of *n*-butylparaben conducted by Yamamoto et al [10] revealed the low efficiency of the process: the post-treatment aqueous concentration remained as high as 90% of the initial concentration ($C_0 = 5.15\cdot10^{-7}$ M) after 50 h exposure. Photolysis by UVC irradiation (254 nm) also was found to be inefficient, with a quantum yield equal to only 0.003 [12]. Far better results were obtained applying advanced oxidation processes. The rate constant for reaction of hydroxyl radicals with BP has a value on the order of $4.8\cdot10^{9}$ dm^3 mol^{-1} s^{-1} [13]. BP reaction with singlet oxygen generated during photosensitized oxidation also leads to the target compound decay [14].

Further investigation concerning BP decay methods is required. The main stress should be placed on compound degradation from natural waters. The main goal of our study was the investigation of how natural water influences BP degradation by UVC irradiation, H_2O_2/UV and photosensitized oxidation.

Materials and methods

Chemicals

Butylparaben (> 99%) (BP), humic acid, *tert*-butanol and sodium azide (99%) were purchased from Fluka, hydrogen peroxide (30%) from POCH, Poland, aluminium *phthalocyanine chloride* tetrasulfonic acid (mixture of regioisomers, PC) from Frontier Scientific and *Meso-tetra(4-sulphonatophenyl)porphin* (TPPS) from Sigma-Aldrich, and used as received. Water was purified using a Millipore Milli-Q Plus System (> 18.2 MΩ).

Sample preparations

Two basic matrices for preparation of BP solutions were used: Milli-Q water and *natural water* (NW). The acidity of the Milli-Q water solution was adjusted by adding phosphate buffer: Na_2HPO_4 - KH_2PO_4 (p.a. POCH, Poland). For more details, see [12, 14]. Natural water samples were collected in June 2009 from the Sulejow Reservoir, situated in central Poland in the middle course of the Pilica River. Water for chemical analyses was filtered through Whatman GF/F (0.45 μm) filters and stored at 4°C before use. The characteristics of NW are shown in Table 1.

Table 1

Characteristic data of natural water (Sulejow Reservoir)

Parameter		Value
pH		8.11
DOC [mg dm^{-3}]		6.85
Cations [mg dm^{-3}]	Li^+	0.003
	Na^+	6.509
	NH_4^+	0.044
	K^+	9.795
	Mg^{2+}	0.969
	Ca^{2+}	34.024
Anions [mg dm^{-3}]	F^-	0.112
	Cl^-	12.343
	NO_2^-	0.025
	NO_3^-	0.46
	Br^-	0.007
	PO_4^{3-}	0.003
	SO_4^{2-}	21.727

Irradiation experiments

Two experimental setups were used, with UVC or xenon arc lamps as a source of light. For UVC direct photolysis and the H_2O_2/UV system, low pressure (LP) lamps (Luzchem) emitting mainly at the wavelength $\lambda = 254$ nm were employed. The tested solutions were irradiated in a merry-go-round device with quartz test tubes (10 cm^{-3}), placed between two exposure panels, each of them consisting of three 7.2 W lamps. Calculated on the basis of actinometric experiments with uranyl oxalate [15], the photon flux rate entering the reaction space equaled $1\cdot 10^{-5}$ einstein dm^{-3} s^{-1}.

For photosensitizing oxidation experiments an immersion xenon arc lamp (XBO, 100 W, Osram) located in a quartz well with cooling jacket was used. The lamp was surrounded by five plate reactors ($V = 0.1$ dm^3), each placed 11 cm from the light source. A single reactor consisted of two glass plates (10 cm × 6 cm) bound with silicone seal in such a way that the distance between the inner surfaces of the plates was 0.3 cm. The tested solutions were aerated and agitated by gas bubbling.

BP solutions at a concentration of $8\cdot 10^{-5}$ mol dm^{-3} in distilled water (buffered in order to obtain pH 8) and in natural water were used. For BP degradation analysis in the H_2O_2/UV system an experimentally determined optimal amount of hydrogen peroxide equal to 0.01 mol dm^{-3} [12] was added to the reaction solution. TPPS and PC at their optimal concentration ($C_0 = 2\cdot 10^{-5}$ M) [14] were used as a sensitizers.

Analytical methods

BP decay in reaction solution was monitored by HPLC-UV using a Waters apparatus. Analysis was performed with a Waters Nova-Pak C_{18} column (3.9 mm × 150 mm) using mobile phase consisting of a degassed mixture of methanol and water acidified with 0.01% orthophosphoric acid at a constant flow 1 cm^3 min^{-1}. The details of HPLC analysis for BP are reported elsewhere [12, 14]. UV spectra were recorded on a Unicam UV 300 spectrophotometer. The *dissolved organic carbon* (DOC) measurements were performed on a HACH IL 550TOC-TN apparatus. The ion concentrations were determined by an ion chromatograph (Dionex model ICS) on an IonPac CS18 (for cations) and an IonPac AS18 (for anions).

Results and discussion

For studies on photochemical degradation, the absorption spectrum of the target compound and lamp emission spectra are important factors. Figure 1 presents BP and NW absorption spectra at pH equal to about 8, overlayed against emission spectra of arc xenon and UVC lamps. Both BP and natural water constituents absorb light in the lamps' emission ranges, what is necessary for photolysis to take place. In alkaline solution BP absorbs at two wavelengths, corresponding to undissociated particles with maxima at λ = 256 nm and to the BP anionic form at λ = 297 nm.

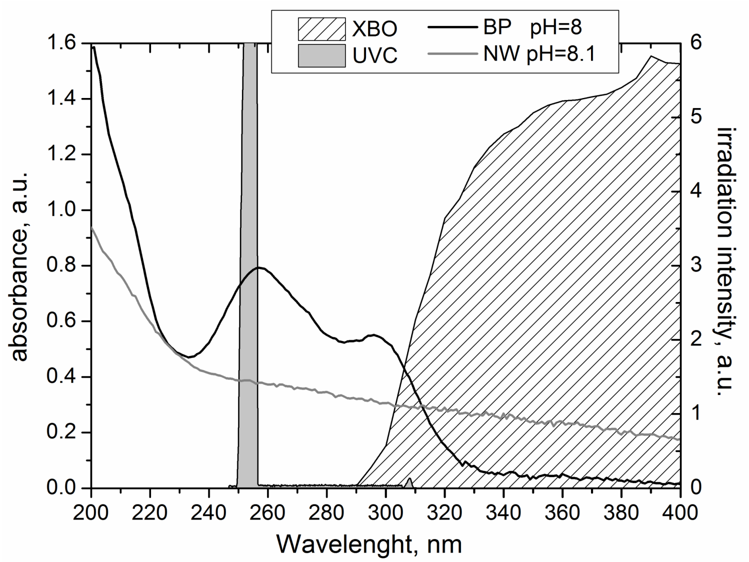

Fig. 1. Absorption spectra of BP (pH = 8, $C_{BP} = 8\cdot10^{-5}$ M) and natural water overlayed against emission spectra of xenon (XBO) and UVC lamps used in experiments

Experiments with low pressure lamp

Figure 2 shows the relative changes of BP concentration during photolysis (Fig. 2A) and in the H_2O_2/UV system (Fig. 2B). The influence of dissolved organic matter on direct photolysis of BP was negligible. Moreover, the additional amounts of humic acids (4.4 mg dm^{-3}) or nitrate(V) (4 mg dm^{-3}), did not influence BP degradation rate (Fig. 2A).

Many aquatic constituents, such as humic acids (HA) and NO_3^- can have an influence on compound degradation course. Dual effect of HA and Cl^- presence in water solution was observed - they may as well promote as inhibit reaction course [16]. In the presence of dissolved organic matter and NO_3^- in water, the generation of additional $^{\bullet}OH$ under light conditions can take place [17]. However, the photolysis of solutions containing nitrates in the presence of the hydroxyl radical scavenger (*tert*-butanol) indicated that species capable of increasing the reaction rate are not generated. It can be explained by the low radiation absorption, at λ = 254 nm, of NO_3^- [18]. Moreover, Gloslan et al [19] found that UVC photolysis do not lead to organic matter degradation.

BP degradation in H_2O_2/UV system (Fig. 2B) can take place through direct photolysis or reaction with hydroxyl radicals generated during hydrogen peroxide photolysis. A slight increase of reaction rate under natural water conditions in comparison with decay in pure water was observed. Degradation in water from Sulejow Reservoir can be slightly accelerated by species generated as a result of dissolved organic carbon photolysis or its reaction with H_2O_2.

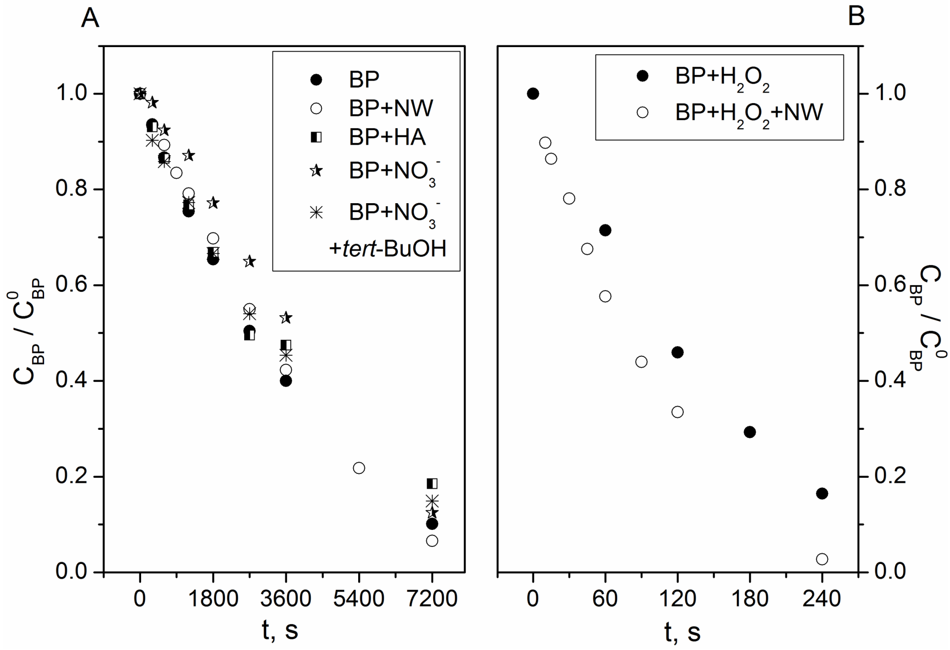

Fig. 2. Changes of relative BP concentration during degradation in natural water (NW) solution and in pure water without and with the additives: humic acid (HA, 4.4 mg dm^{-3}), nitrate(V) ions (NO_3^-, 4 mg dm^{-3}), NO_3^- and *tert*-butanol (0.1 mol dm^{-3}) and in natural water (NW) solution under UVC lamp irradiation (A). Evolution of relative BP concentration in H_2O_2/UV system as a function of irradiation time under buffer or natural water conditions (B). $C_{BP}^0 = 8\cdot10^{-5}$ M; $E_0 = 1\cdot10^{-5}$ einstein dm^{-3} s^{-1}, pH = 8

Experiments with xenon arc lamp

For BP photosensitized oxidation two sensitizers: TPPS and PC with different durability but similar quantum yield of singlet oxygen generation were used [20]. Absorption of UV radiation by sensitizer results in excited state, which initiates organic compounds degradation. Excited sensitizer can react either with oxygen, which leads to singlet oxygen or superoxide radical anion generation or directly with target compound.

An increase of photosensitized oxidation in natural water from Sulejow Reservoir in comparison with buffered pure water solution (pH = 8) was observed (Fig. 3). As shown in Figure 3A, after two hours of irradiation in the presence of TPPS 77% conversion in pure water and 93% of BP initial concentration reduction under natural water conditions was achieved. Also in photosensitized oxidation with PC as a sensitizer, increase of BP depletion in natural water (80%) in comparison with pure water solution (66%) was observed (Fig. 3B).

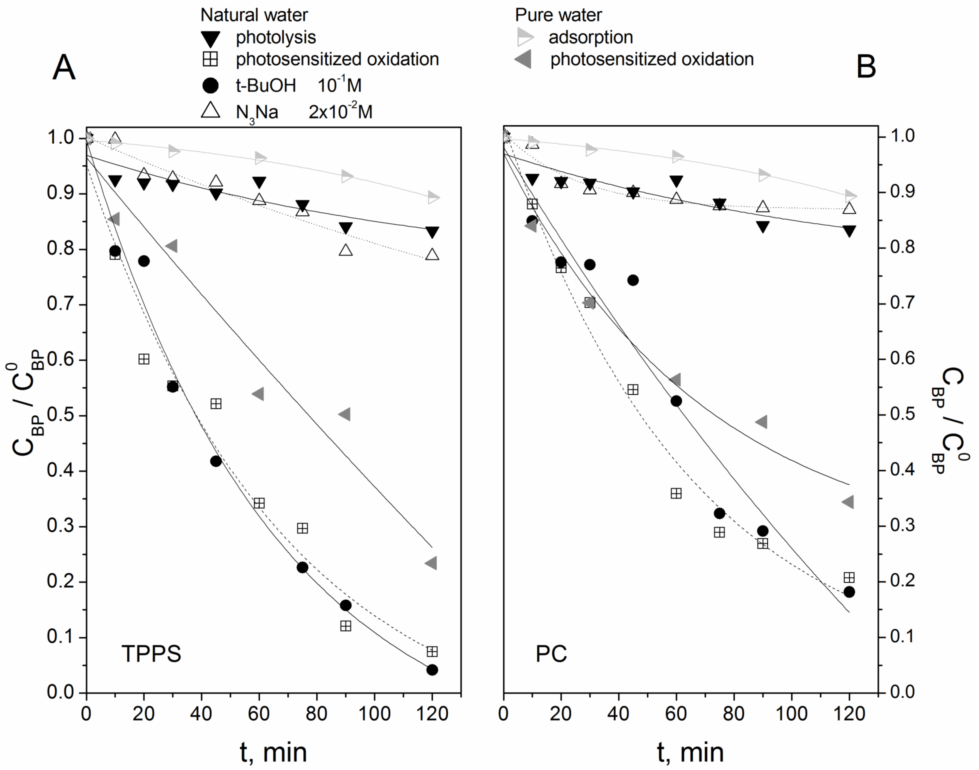

Fig. 3. Changes of the BP relative concentration during photosensitized oxidation in natural water (pH = 8.1) and buffer pure water (pH = 8) solution in presence of TPPS ($C^0 = 2\cdot10^{-5}$ mol dm^{-3}) (A) and PC ($C^0 = 2\cdot10^{-5}$ mol dm^{-3}) sensitizers. $C_{BP}^0 = 8\cdot10^{-5}$ M; $E_a = 1.30\cdot10^{-6}$ einstein dm^{-3} s^{-1}

An important factor which needs to be taken into consideration in the case of our photosensitized oxidation experiments was reactors construction, where the adsorption of BP on silicone seal can occur. Preliminary studies showed that BP concentration decrease caused by its adsorption on silicone seal equal about 10% after 2 hours (Fig. 3). Moreover, BP anionic forms undergo direct photolysis under xenon arc lamp irradiation (Fig. 1).

Therefore, during photosensitized oxidation the reduction of BP concentration in pure and natural water should be diminished by 15÷18%.

The difference in the degree of BP degradation during photosensitized oxidation (about 15%) was probably caused by substances present in natural water, which increase BP decay. It is known that absorption of ultraviolet and visible radiation by dissolved organic matter (DOM) in aerated solution leads to a *reactive oxygen species* (ROS) such as singlet oxygen ($^1O_2$), superoxide radical anion ($^{\bullet}O_2^-$) hydroxyl radicals ($^{\bullet}OH$) and peroxyl radicals ($ROO^{\bullet}$) generation [21, 22]. These species participate in the BP degradation causing an increase of the reaction rate.

Experiments conducted during photosensitized oxidation in the presence of hydroxyl radical scavenger - *tert*-butanol permitted to exclude the participation of hydroxyl radicals. However, experiments with addition of sodium azide - physical quencher of singlet molecular oxygen indicated that singlet oxygen plays a dominant role in BP degradation (Fig. 3).

DOM, in particular humic acids, are known as a natural sensitizer and plays a key role in the intensification of BP degradation. Nevertheless, it was estimated that only from 1 to 3% of the absorbed by humic substances solar radiation energy is used for singlet oxygen generation [23]. Therefore, we can assume that also other constituents present in Sulejow Reservoir water could accelerate BP degradation.

Conclusions

Analysis of experimental results allowed us to come to the following conclusions:

1. The most efficient BP degradation method was the reaction in the H_2O_2/UV system.
2. The presence of natural constituents in water taken from Sulejow Reservoir did not influence on direct photolysis by UVC and slightly increase BP depletion rate in H_2O_2/UV system.
3. The course of BP photosensitized oxidation was accelerated under natural water conditions.
4. BP degradation during photosensitized oxidation, both in pure water and in natural water from Sulejow Reservoir, is a result of reaction with singlet oxygen.

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FOTODEGRADACJA KSENOBIOTYKU *n*-BUTYLOPARABENU W WODZIE Z ZALEWU SULEJOWSKIEGO

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Abstrakt: W pracy przedstawiono badania degradacji *n*-butyloparabenu, ksenobiotyku zakłócającego pracę gruczołów wydzielania wewnętrznego w roztworach wody destylowanej i w wodzie naturalnej, pochodzącej z Zalewu Sulejowskiego. Reakcję rozkładu prowadzono metodami fotochemicznymi na drodze fotolizy promieniowaniem lampy UVC, bez i w obecności nadtlenku wodoru oraz poprzez fotosensybilizowane utlenianie z użyciem dwóch sensybilizatorów i lampy ksenonowej imitującej promieniowanie słoneczne. Przebieg fotolizy oraz utleniania w układzie H_2O_2/UV prowadzony w buforowanej wodzie destylowanej i w wodzie naturalnej praktycznie się nie różni. Natomiast proces fotosensybilizowanego utleniania w wodzie naturalnej przebiega ze zwiększoną szybkością, pozwalając uzyskać w tym samym czasie reakcji o około 15% wyższą redukcję zanieczyszczenia.

Słowa kluczowe: ksenobiotyki, butyloparaben, fotoliza, układ H_2O_2/UV, fotosensybilizowane utlenianie, woda naturalna

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THERMODYNAMICS OF REACTIVE DYE ADSORPTION FROM AQUEOUS SOLUTION ON THE ASHES FROM CITY HEATING STATION

TERMODYNAMIKA ADSORPCJI REAKTYWNYCH BARWNIKÓW Z ROZTWORÓW WODNYCH NA POPIOŁACH Z CIEPŁOWNI MIEJSKIEJ

Abstract: This paper describes the adsorption thermodynamics of textile reactive dyes from aqueous solution on the waste ashes formed by burning brown coal at a city heating station. The values of thermodynamic parameters are the actual indicators for practical application in the adsorption process. Based on characteristic diagrams the thermodynamic parameters, enthalpy and entropy of adsorption are determined, and based on those data the Gibbs's free energy changes were determined. In all cases, there is a negative sign of the thermodynamic parameters. Entropy change (–2 to –3 J/K·mol) increases with increasing initial concentration of the adsorbate and decreases with increasing amount of adsorbent, suggesting a decrease in disordered system at the interface of solid - solution during the adsorption of dye on the ashes. Free energy (–1.7 to 5 kJ/mol) decreases with the concentration of adsorbate discontinuously but continuously with increasing temperature, which is associated with spontaneous nature of the process. Small negative values of enthalpy change (–2 to –6 kJ/mol), point to the physical nature and the energy stability of the reactive dyes adsorption by ashes.

Keywords: thermodynamics, reactive dye, adsorption, ashes

The first major challenge in the selection of favorable adsorption sorbents that are the most promising, mainly is due to higher capacity and adsorption rate, high selectivity and low prices. The next genuine challenge is to clearly identify the mechanism of adsorption, especially the interactions involved at contact area adsorbent/adsorbate. Absorption processes, where the waste products (ashes) are used for the adsorption, can be very useful and effective, but above all make simple and inexpensive materials as opposed to the conventional processes of the wastewaters refinements.

Properties of the adsorption and equilibrium data, known as adsorption isotherms, describe how contaminants react with adsorbents, and thus are critical to the choice and wider application [1-4]. A precise mathematical description of equilibrium adsorption

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capacity is indispensable for the accurate prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent systems (or for different experimental conditions) [5, 6].

Mathematical modeling is undoubtedly a valuable tool for analysis and the concept of adsorption systems and for theoretical evaluation and interpretation of thermodynamic parameters as well. However, the isotherm can match the experimental data under one set of conditions but can be prone to total failure under another one. In addition, none of the existing model is fully applicable. This is understandable taking into account the hypotheses associated with their deviation.

Reactive dyes are typically based on the nitrogen chromophors combined with the various types of the reactive groups, for example vinyl sulphone, chlorotriasine, trichloropirimidine, difluorochloropirimidine. Azo-reactive dyes are characterized by the presence of one or more azo bonds (-N=N-). Almost 45% annually produced textile dyes, belong to the reactive class because of the intensive usage this kind of dyes for dyeing of cellulose, wool and viscous-rayon fibers.

Reactive dyes are identified as problematic agents in the wastewaters because they are water-soluble. In the wastewater, they are found in larger quantities than the other kinds of dyes and mainly in the hydrolyzed form, so they cannot be so easily removed by the systems of the conventional treatments [7]. These dyes are more problematic that any other dyes and must be removed from the wastewaters completely [8]. The removal of these dyes from the wastewaters is a main challenge of the natural environment protection and there is a constant need of the efficient process, which can solve the problem of the dyed wastewater.

Reactive dye applied in this paper belongs to the group of anionic dye due to the sulfo group in its structure. It is a dye bifunctional reactive dyeing of cellulosic fibers, or continuous processes of exhaustion. Dye is especially known for its high reliability, simple dyeing and great patina color. It was chosen because of the presence of metal atoms (Cu) in its structure, and by extension the known circumstances relating to metals and environmental pollution problems in maintaining or preventing leakage of metal compounds in the environment.

Materials and methods

As adsorbent bottom ash, from local power plants obtained by brown coal combustion, was used. After collecting and drying, sieving to the particle size of 0.5 mm is carried out. Crude ash was abundantly rinsed with distilled water, dried in the air, again sifted and used in the experiment. In the process of adsorption, the reactive dye, C.I. Reactive Blue 221 from the textile factory (hereafter Reactive Blue) was used.

Adsorption procedure

Adsorption test was performed in a glass Erlenmeyer flask in which the adsorbent is suspended in the solution dye-adsorbate. The Erlenmeyer flasks are placed on the shaker - at 150 rpm at a certain temperature and kept in a specified time. The amount of ash was varied in the amount of 1 to 4 g, while the solution of 100 cm^3, contained concentrations of dye, 10, 30, 50, 70 and 100 mg/dm^3. Processing time, with constant stirring, was 5, 10, 20, 30, 45 and 60 min, while pH varied from 2 to 12, was regulated by adding 1 M solution of sulfuric acid or sodium hydroxide.

The above-mentioned dye concentrations were used because they generally correspond to residual amounts of dyes in the solution after the wool textiles dyeing. Practically, in the experiment, commensurable concentration of pure dye with no additives that typically go with dyeing. It was found that equilibrium adsorption time of the dye on the ashes is achieved in 60 min, with the extension of time of treatment the adsorption did not significantly alter.

Upon completion of the adsorption, the solutions of dye and ash are passed through a filter paper. What follows is the determination of the absorption solution on the spectrophotometer UV-VIS spectrophotometer (*Cary 100 Conc UV-VIS, Varian*) at $\lambda = 565$ nm.

SEM (*scanning electron microscopy*) measurements were conducted on the device *VEGA TS 5130mm (TESCAN)* using a detector for secondary electrons. Ash used is a relatively fine-bulk material with heterogeneous particles of widespread shapes and forms that come from agglomerates of individual minerals, in general, less than 5 μm in size. Micrograph in Figure 1 shows a view with 5000x magnification.

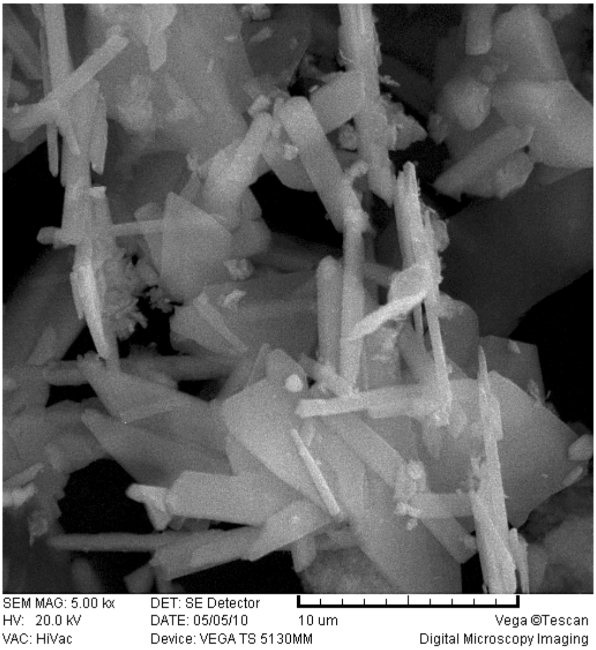

Fig. 1. Micrograph of the applied adsorbent

Diffraction measurements were performed on the *Bruker D8 Advance diffractometer* in θ/θ "scan-step" mode in the range of diffraction angles 2θ from 10° to 90° in steps of 0.05° and a total exposure of 5 s per step. On the diffractogram obtained using, the *EVA software package v.9.0* into which is incorporated crystallographic database PDF-2, phase identification of an adsorbent was carried out, semi-quantitative phase analysis was done and the results of this analysis are shown in Figure 2.

X-ray spectrum strips of the adsorbent (Fig. 2) reveal the presence of minerals, mainly dominated by gypsum and quartz, followed by calcite and aluminium hydrogen sulfate, and finally with a share below 10% coming ferchilidit, melanterit, oldhamit and iron sulfate.

As the calcium and silicon compounds (sulfate and oxide) are present for the most part (together they have over 50%) and how it is known that these elements are more stable than in silicate compounds than as the oxides, it leads to the conclusion that there was no combustion at high temperatures [9].

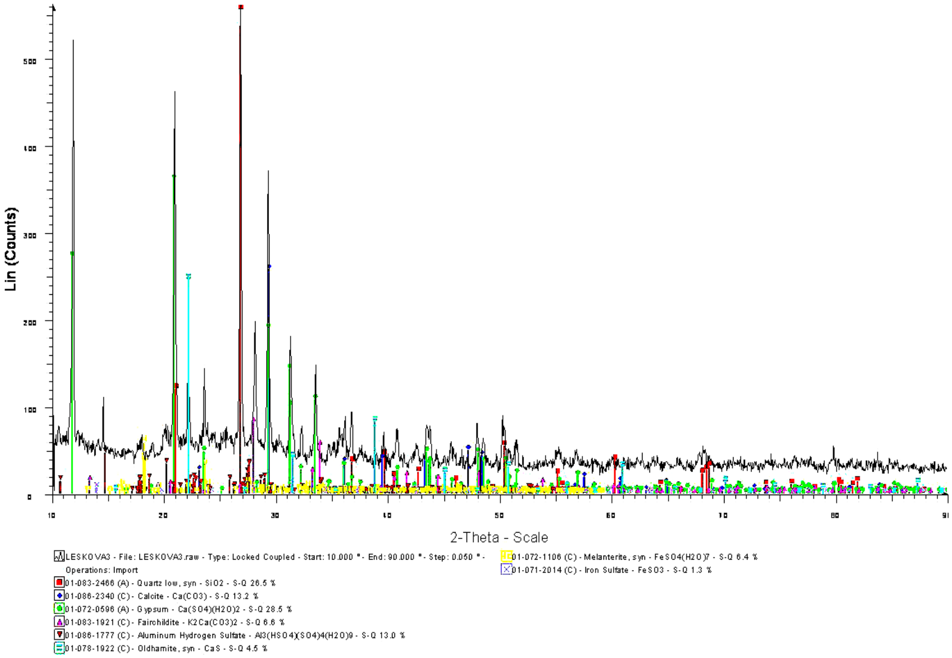

Fig. 2. X-ray diffraction diagram of the applied adsorbent

Results and discussion

The values of thermodynamic parameters of the actual indicators for practical application process were determined. In some adsorption processes, entropy and energy were considered and must be taken into account in defining the process that occurs spontaneously.

Temperature effect on the adsorption

Temperature effect on the quantity if the adsorbed dye by the unit of ash mass was studied in the temperature range from 20÷60°C at the changing starting concentrations of dye (Fig. 3). The diagrams in this Figure bring the result for the maximal starting concentration of dye and the smallest quantity of ash, 1 g. The results for the other applied dye concentrations and adsorbent quantity were not shown because there were no bigger visual variations.

It was deduced that higher temperature simplifies dye removal with adsorption on an adsorbent. The data also shows that the temperature effect is not so significant because the changes were inconsiderable, in comparison with the adsorption at 20 and 60°C.

The amplification of the adsorption with temperature can be assigned to the increased number of active surface locations that are available for adsorption on every adsorbent, porosity and the overall cubage of the pores of the adsorbent. The intensity of the adsorption can also derive from the decreased thickness of the limiting layer, which surrounds the adsorbent with the temperature when the resistance, against transmission of adsorbent mass in the limiting layer, is reduced. This can also be the result of an increase in dye-molecule mobility with an increase of their kinetic energy and increased diffusion speed inside of the particles of adsorbents due to the temperature increase [10].

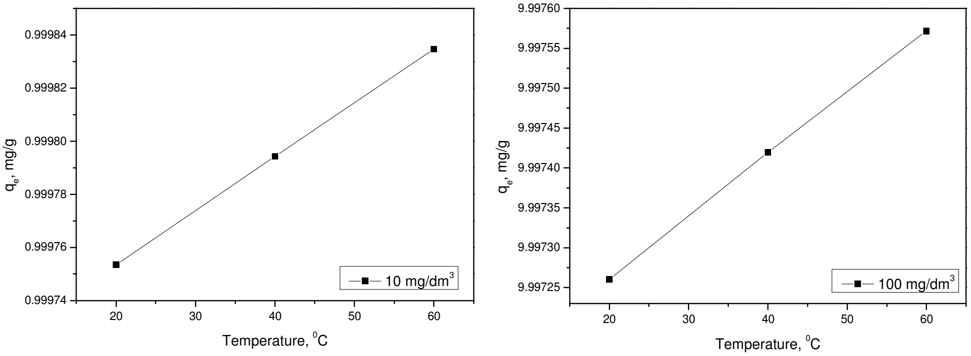

Fig. 3. Temperature effect on the amount of the adsorbed Reactive Blue by the unit of the mass of ash (q_e) for the lowest (left) and highest (right) starting concentration

The thermodynamic of adsorption

Thermodynamic parameters for adsorption systems were calculated using the following equation [11, 12]

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{R \cdot T} \tag{1}$$

$$\Delta G = \Delta H - T \cdot \Delta S \tag{2}$$

where: k_2 - the rate constant of adsorption of the second order [g/mg·min]; T - temperature [K], k_b - Boltzmann's constant ($1.38065 \cdot 10^{-23}$ J/K); h - Planck's constant ($6.626 \cdot 10^{-34}$ J·s); ΔS - change in entropy [J/K·mol]; R - universal gas constant (8.314 J/K·mol); ΔH - change of enthalpy [J/mol]; ΔG - change of Gibbs free energy [J/mol].

Graph of $\ln(k_2/T)$ versus 1/T gives a straight line with a slope - $\Delta H/R$ and intercept $[\ln(k_b/h) + \Delta S/R]$, from which the change in enthalpy and entropy was calculated.

Figures 4 and 5 are diagrams for Reactive Blue and all amounts of adsorbent based on which (slope and intercept) are determined the basic thermodynamic parameters, enthalpy and entropy of adsorption, and based on those determined the change of Gibbs's free energies.

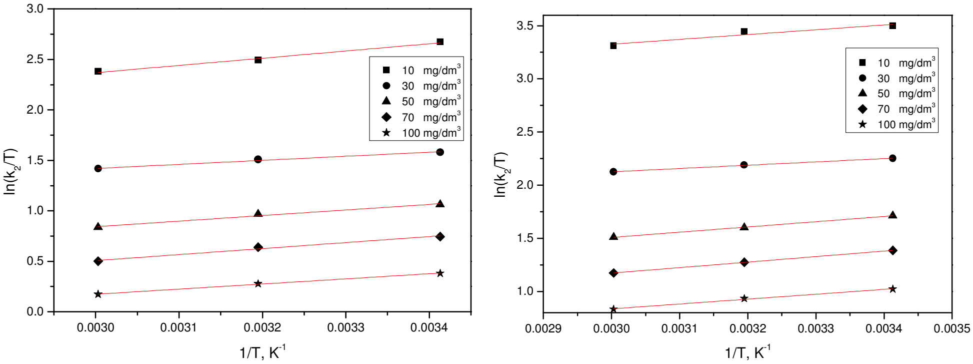

Fig. 4. Ln (k$_2$/T) vs 1/T for adsorption of Reactive Blue on ashes (ashes: 1 g/100 cm^3 - left, 2 g/100 cm^3 - right)

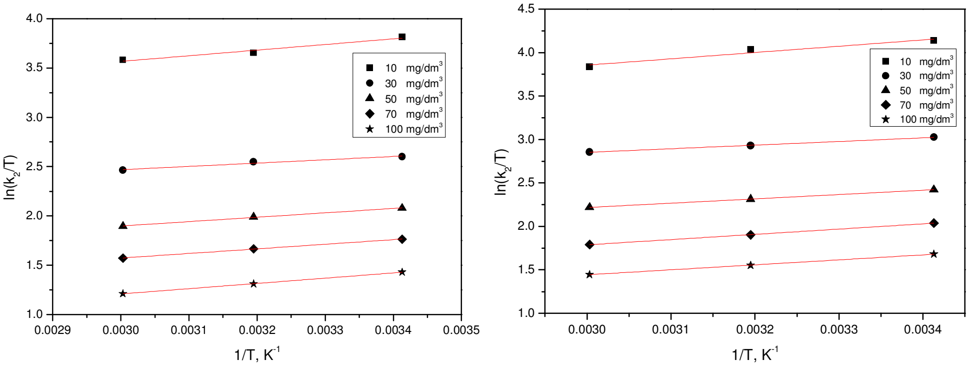

Fig. 5. Ln (k$_2$/T) vs 1/T for adsorption of Reactive Blue on ashes (ashes: 3 g/100 cm^3 - left, 4 g/100 cm^3 - right)

Tables 1-4 brings specific values of the determined thermodynamic parameters, entropy, enthalpy and free energy for applied dye, any quantity of adsorbents, initial concentrations and applied temperatures.

Table 1

Thermodynamic parameters of adsorption of Reactive Blue on ashes (1 g/100 cm^3)

Dye concentration [mg/dm^3]	**ΔS [J/mol·K]**	**ΔH [kJ/mol]**	**ΔG [kJ/mol]**		
			20°C	**40°C**	**60°C**
10	–2.831	–5.955	–5.126	–5.069	–5.012
30	–2.832	–3.348	–2.518	–2.461	–2.405
50	–2.955	–4.588	–3.722	–3.663	–3.604
70	–3.011	–4.927	–4.044	–3.984	–3.924
100	–3.020	–4.224	–3.339	–3.279	–3.218

Table 2

Thermodynamic parameters of adsorption of Reactive Blue on ashes (2 g/100 cm^3)

Dye concentration [mg/dm^3]	**ΔS [J/mol·K]**	**ΔH [kJ/mol]**	**ΔG [kJ/mol]**		
			20°C	**40°C**	**60°C**
10	–2.621	–3.760	–2.992	–2.939	–2.887
30	–2.714	–2.590	–1.795	–1.740	–1.686
50	–2.854	–4.102	–3.266	–3.209	–3.152
70	–2.904	–4.309	–3.458	–3.400	–3.342
100	–2.924	–3.835	–2.979	–2.920	–2.862

Table 3

Thermodynamic parameters of adsorption of Reactive Blue on ashes (3 g/100 cm^3)

Dye concentration [mg/dm^3]	**ΔS [J/mol·K]**	**ΔH [kJ/mol]**	**ΔG [kJ/mol]**		
			20°C	**40°C**	**60°C**
10	–2.635	–4.748	–3.976	–3.923	–3.871
30	–2.682	–2.795	–2.009	–1.955	–1.902
50	–2.791	–3.714	–2.897	–2.841	–2.785
70	–2.837	–3.883	–3.052	–2.995	–2.938
100	–2.904	–4.426	–3.575	–3.517	–3.459

Table 4

Thermodynamic parameters of adsorption of Reactive Blue on ashes (4 g/100 cm^3)

Dye concentration [mg/dm^3]	**ΔS [J/mol·K]**	**ΔH [kJ/mol]**	**ΔG [kJ/mol]**		
			20°C	**40°C**	**60°C**
10	–2.655	–6.025	–5.247	–5.193	–5.140
30	–2.665	–3.469	–2.688	–2.635	–2.581
50	–2.771	–4.143	–3.331	–3.275	–3.220
70	–2.861	–5.021	–4.183	–4.126	–4.069
100	–2.890	–4.750	–3.903	–3.845	–3.788

According to the Tables 1-4, entropy increases with increasing initial concentration of adsorbate and is generally decreased with increasing amount of adsorbent. Reorientation or restructuring of water around the molecules of a dye is very unhelpful as far as the entropy is concerned, since it disturbs the existing water structure and imposes a new, ordered structure at the nearby water molecules. Energy released during the adsorption process compensates for the loss of entropy of adsorbed molecules, the stronger the forces, the more energy is released [11, 13].

As it can be stated that entropy can be thought of as a measure of "linked" energy of a closed material system, ie energy which is in contrast to "free", it can not be converted into work, the change of the negative entropy (approximately - 3 J/K·mol) correspond to the reduction of degrees of freedom of the adsorbed dyes, ie suggests that disordered system is decreased at the interface solidyl - solution during the adsorption of a dye on the ashes [13].

Free energy decreases continuously with an increasing temperature, whereas an increase concentration of adsorbent grows from 2 g/100 cm^3. By increasing the mass of ash free energy changes discontinuously, showing a close and the highest values for 1 and 4 g of an adsorbent. Since the adsorption reaction is feasible only if the overall Gibbs free enthalpy change is negative, then minus values of free energy indicate the feasibility and spontaneous nature of the process, ie favours the adsorption of the applied paint at 20, 40 and 60°C. This is to confirm the feasibility of the process and spontaneous nature of adsorption at the applied temperatures with high affinity of the molecules for the surface of the adsorbents.

Small negative values of enthalpy change (between –2 to –6 kJ/mol) indicate physical nature the adsorption, mostly, including weak exothermic attractive force, and that the process is energy-stable. An enthalpy change continuously rises from the concentration of adsorbent increases ranging from 2 g/100 cm^3. With the amount of adsorbent from 1 g/100 cm^3, it has values similar to those, which occur, in the maximum amount of adsorbent. With the increased concentration of dye, enthalpy change mainly rises from adsorbate concentration of 30 mg/dm^3. These phenomena can be explained with the fact that in the adsorption process the break of the link between adsorbate molecules and adsorbent surface occurred [14].

Energy released during adsorption is manifold during the measuring in the range of energies that originate from adsorption by different forces, for example - Van der Waals 4÷10 kJ/mol, hydrophobic connection 5 kJ/mol, hydrogen bond 2÷40 kJ/mol, coordinating ties about 40 kJ/mol, dipole connection 2÷29 kJ/mol, chemical bond about 60 kJ/mol. In our case the change of enthalpy during adsorption on the ashes of dye, suggests that the adsorption reaction system of the dye largely excludes the Van der Waals connections, hydrophobic interactions and, to a lesser extent, dipolar forces, since these interactions carry smaller amounts of energy [15].

Conclusions

Adsorption has certain advantages over conventional treatment processes because it eliminates the complete molecule, not leaving the parts in water. This is especially important for dyes containing metals, where the linked metals (eg Cr, Co, Cu) remained in the wastewater and perhaps even more harmful non-complex form.

Removal of reactive dyes with ash was investigated under various conditions. Based on these results, we can say that the ashes of district heating are efficient adsorbent for removing metal-complex dye from aqueous solutions with a reasonable tendency of use in industrial environments. The characterization of other, similar in nature, solid waste materials, can help in clarifying the interaction adsorbate - adsorbent, which leads to greater efficiency and optimization of the adsorption, as an environmentally very acceptable procedure.

Based on experimental results can be drawn the following conclusions:

- **Negative values of free energy changes** indicate the spontaneous nature of adsorption: $\Delta G = -2.4$ to –5.1 kJ/mol for 1 g of ash and all the applied temperatures; –1.7 to –3.4 kJ/mol for 2 g ash and all used temperatures; –1.9 to –3.9 kJ/mol for 3 g ashes and all the applied temperatures; –2.5 to –5.2 kJ/mol for 4 g ashes and all the applied temperatures.
- **Negative values of free enthalpy changes** show that the adsorption process is taken to include the weak attractive forces that are exothermic: $\Delta H = -3.3$ to –5.9 kJ/mol for 1 g of ash, –2.6 to –4.3 kJ/mol for 2 g ash; –2.8 to –4.7 kJ/mol for 3 g ash, –3.5 to –6.0 kJ/mol for 4 g of ash.

- **Negative values of free entropy changes** indicate a reduction of unstable systems at the interface solidyl - solution during the adsorption; ΔS = –2.8 to –3.0 J/mol·K for 1 g of ash, –2.6 to –2.9 J/mol·K to 2 g of ash, –2.6 to –2.9 J/mol·K for 3 g ash, –2.6 to –2.9 J/mol·K for 4 g ash.
- **Based on the thermodynamic data**, it can be concluded that dominates the physical dye adsorption in relation to chemisorption. Precisely, certain anomalies (several cases) in some indicators may indicate an error and the existence of, for example, chemical interactions in the system.

Undoubtedly, many offer cheap adsorbents used for commercial purposes for the future. Based on this study, adsorbent based on ash shows good ability to remove certain types of reactive dyes. Naturally, there are some limitations and problems. Despite numerous publications on low-cost adsorbents, for now there is little information contained in the full study of the individual adsorbents. Variable chemical nature of wastewater in a different period may reinforce the problem of the dye of specific adsorbents more. For the design of adsorption system, it is necessary to understand the mechanism of adsorption process in order to achieve optimization. It is also important to understand the adsorption mechanism for the efficient activation and regeneration of adsorbents. Although much has been achieved in the field of low-cost sorbents, it is still much work necessary (i) to predict the effect of adsorption process for removing dye from actual industrial wastewater under operating conditions, (ii) to better understand the adsorption mechanism and (iii) use of low-cost adsorbents in industrial scale.

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TERMODYNAMIKA ADSORPCJI REAKTYWNYCH BARWNIKÓW Z ROZTWORÓW WODNYCH NA POPIOŁACH Z CIEPŁOWNI MIEJSKIEJ

Abstrakt: W pracy opisano termodynamikę adsorpcji reaktywnych barwników tkanin z roztworu wodnego na popiołach powstających jako odpad w wyniku spalania węgla brunatnego w miejskich ciepłowniach. Wartości parametrów termodynamicznych są właściwymi wskaźnikami służącymi praktycznemu opisowi procesu adsorpcji. Na podstawie odpowiednich diagramów zostały określone następujące parametry termodynamiczne: entalpia i entropia adsorpcji, a na podstawie tych danych określono zmiany energii Gibbsa. We wszystkich przypadkach wartości parametrów termodynamicznych były ujemne. Różnica entropii (–2 do –3 J/K·mol) rośnie wraz ze wzrostem początkowego stężenia adsorbatu i zmniejsza się wraz ze zwiększającą się ilością adsorbentu, co sugeruje zmniejszenie nieuporządkowania układu na granicy fazy stałej i roztworu w trakcie adsorpcji barwnika na popiołach. Energia swobodna (–1,7 do 5 kJ/mol) zmniejsza się w sposób nieciągły wraz ze stężeniem adsorbatu, ale w sposób ciągły wraz ze wzrostem temperatury, co jest związane ze spontanicznym charakterem procesu. Małe, ujemne wartości zmiany entalpii (–2 do –6 kJ /mol) wskazują na fizyczny charakter i stabilność energii adsorpcji barwników reaktywnych na popiołach.

Słowa kluczowe: termodynamika, barwniki reaktywne, adsorpcja, popiół

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CHROMATOGRAPHIC, SPECTROPHOTOMETRIC AND ELECTROCHEMICAL METHODS IN DETERMINATION OF BIOGAS COMPONENT

METODY CHROMATOGRAFICZNE, SPEKTROFOTOMETRYCZNE I ELEKTROCHEMICZNE W OZNACZANIU SKŁADU BIOGAZU

Abstract: Biogas is a mixture of many gasses to which the main contribution of two thirds is brought by methane (CH_4) and one third by carbon dioxide (CO_2), while the other components including steam occur in trace amounts. Effective control of the process of fermentation is based on controlling the following parameters: type and amount of the substrates supplied, temperature of the process, pH value, amount of short-chain fatty acids, the degree of filling of the fermentation tank and the chemical composition of the gas obtained. In this study the measurements of quantitative composition of biogas made by a popular portable biogas analyser GA2000 were verified by gas chromatography determinations. In the analyser the content of methane and carbon dioxide is made by a spectrophotometric method, while the content of oxygen and hydrogen sulphide is measured electrochemically.

Keywords: biogas, gas chromatography, biogas analyser, verification of measurements

Biogas is produced in a complex biochemical reaction known as fermentation taking place in anaerobic conditions with the involvement of bacteria that decompose organic substances into simple compounds, mainly methane and carbon dioxide. The rate of organic matter decomposition depends on many factors, one of which is temperature. When the process takes place at 10÷20°C it is referred to as psychrophilic fermentation, when at temperatures from the range 32÷42°C it is referred to as mesophilic fermentation and when it takes place in temperatures from the range 48÷55°C - the process is called thermophilic fermentation. Efficient fermentation needs relative humidity of over 50% and pH higher than 6.8. The amount of biogas obtained and its composition depend on the type of waste undergoing fermentation. Great content of organic substances in the waste fermented favours getting biogas with a large content of methane.

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With increasing length of the hydrocarbon chain of the organic substances undergoing fermentation the amount of methane in the biogas obtained increases, as shown in Figure 1 [1].

When the waste subjected to fermentation is liquid manure of pigs or used vegetable oils the biogas obtained can contain even more than 70% of methane [2]. The duration of biogas production also depends on the type of waste undergoing fermentation and ranges from 10 days for grass silage to 121 days for cow stable manure [2].

The typical biogas applications include:

- as a component of gas supplied through the gas network,
- as fuel for motor vehicles,
- as fuel for production of electric energy,
- for production of heat,
- in a number of technological processes, eg in production of methanol.

Table 1 presents the parameters characterising biogas of typical composition, ie containing 55÷70% of methane and 30÷45% carbon dioxide, a fuel [3].

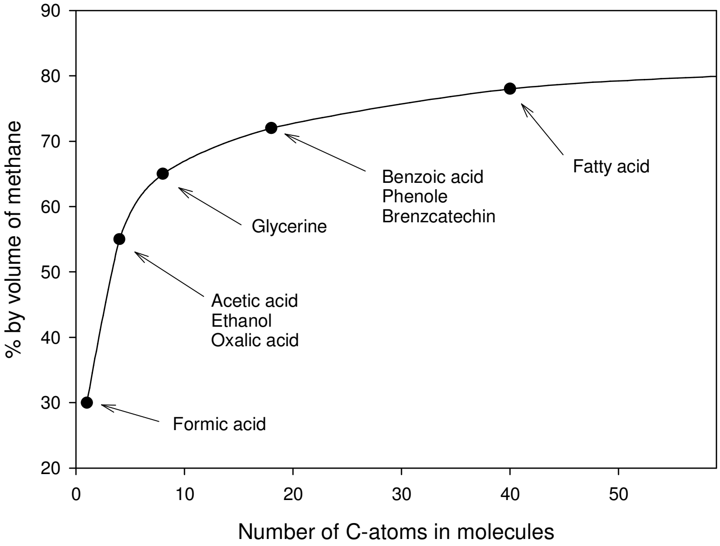

Fig. 1. Correlation between methane [%] in biogas and number of carbon atoms in substrate molecules

Typical composition of biogas and description of their influence on biogas properties and biogas installation performance are given in Table 2 [3].

Not each type of biogas can be used for energy production. The main criterion of biogas for such application is that it must contain at least 40% of methane. For the majority of substrates used, the content of methane is 60÷65% and the content of carbon dioxide is 35÷40%, however, some authors have reported the increase of carbon dioxide content in biogas up to 50÷60% [4]. A higher content of liquid in the bioreactor results in a higher concentration of CO_2 dissolved in water, reducing the level of CO_2 in the gas phase. The higher the temperature during the fermentation process the lower is the concentration of

CO_2 dissolved in water. A higher pressure lead to a higher concentration of CO_2 dissolved in water. As far as the contents of nitrogen and oxygen are concerned, these compounds occur at the ratio of 4:1 and get into the biogas produced at very low productiveness of source, eg at the waste dumping grounds, or during technological processes or they are added on purpose in the amount of 3÷5% [4] to ensure the correct course of biological desulphurisation.

Table 1

General features of biogas

Parameter	Content
Energy content	60÷6.5 kWh m^{-3}
Fuel equivalent	0.60÷0.65 dm^3 oil m^{-3}
Explosion limits	6÷125 biogas in air
Ignition temperature	650÷750°C
Critical pressure	75÷89 bar
Critical temperature	–82.5°C
Normal density	1.2 kg m^{-3}
Smell	Bad eggs
Molar mass	16.043 kg $kmol^{-1}$

Table 2

Typical components of biogas and their effect on biogas and biogas installation performance

Component	Content	Effect
CO_2	25÷50%	- Lowers the calorific value - Causes corrosion if the gas is wet - Increases the methane number and the antiknock properties of engines - Damages alkali fuel cells
H_2S	0÷0.5%	- Corrosive effect in equipment and piping system - Emits SO_2 on combustion
NH_3	0÷0.05%	- Emits NO_x on combustion - Increase the antiknock properties of engines
Water vapour	1÷5%	- Causes corrosion of installation - Products of condensation can cause damage to the engine and choke installation - Risk of freezing of piping systems and nozzles
Dust	> 5μm	- Blocks nozzles and fuel cells
N_2	0÷5%	- Lowers the calorific value - Increase the antiknock properties of engines
Siloxanes	0÷50 mg/m^3	- Act as abrasive material causing damage to the engine

Another important component is hydrogen sulphide (H_2S), whose content determines the biogas quality, although it occurs in trace amounts. Its content should not be too high as already in low concentrations it inhibits the process of decomposition and causes corrosion of the biogas production installation, including power-heat units and water boilers. Many producers of biogas generators admit the content of hydrogen sulphide at a level of 0.05% [3]. It should be also mentioned that a product of H_2S combustion is SO_2, so when biogas is subjected only to combustion in a flare the admitted concentration of H_2S is 0.1% [3]. Biogas also contains small amounts of carbon oxide, not exceeding 0.2%. The concentration of another biogas component ammonia is usually kept at a level below < 0.1 mg m^{-3}. Its amount is closely related to the type of substrates used and in certain biogas samples the concentration of ammonia reached 150 mg m^{-3} [5]. Other impurities met in biogas include chlorine, fluorine and mercaptans, however, their concentration is below 0.1 mg m^{-3} and trace amounts of aromatic hydrocarbons: the concentrations of BTX are below 1 mg m^{-3} and the concentrations of PAH - below 0.01 μg m^{-3} [3]. Important is also the presence of siloxanes getting into the wastewater with cosmetic products, detergents or construction materials. They have deteriorating effect on biogas generators as their combustion in the presence of oxygen leads to formation of silica acting as abrasive material [6].

The above survey of the information on possible impurities of biogas and their effects illustrates the importance of monitoring of the chemical composition of the biogas produced.

Material and methods

Most often the chemical composition of biogas is made with the use of portable analysers whose activity is based on measurements of thermal conductivity, infrared radiation absorption or electrochemical sensors [4]. The choice of particular type of analyser should be made on the basis of its accuracy, selectivity, linearity, range of measurements and sensitivity of the sensors or analytical methods employed. For determination of methane and carbon dioxide, the sensors based on infrared radiation absorption are very effective, whereas for determination of hydrogen, oxygen and hydrogen sulphide more effective are the electrochemical sensors. Analysis of biogas components was made by a portable analyser GA2000 made by Geotech [7]. For determination of methane and carbon dioxide it uses a double beam of infrared radiation and a reference cell. Determination of oxygen, carbon oxide and hydrogen sulphide is made by electrochemical sensor. The device permits determination of methane to the content of 70%, carbon dioxide to 60%, oxide to 25%, carbon oxide and hydrogen sulphide to 500 ppm. The accuracy of indications declared by the producer for CH_4 and CO_2 at their content above 15% is ±3% and for O_2 in the content up to 5% is ±1%. The accuracy of indications declared for H_2S and CO in the range up to 500 ppm is ±10%. According to the producer's recommendations the analyser was periodically subjected to calibration using a certified mixture containing 30% of methane, 20% of carbon dioxide and 100 ppm of hydrogen sulphide. The calibration for oxygen was performed with reference to its content in the air.

Fig. 2. Biogas analyser series GA2000

The analyser GA2000 is equipped with a pump, but because of high overpressure of biogas at the intake sites, the pump was not used. The intake of the biogas sample was continued until getting stabilised indications of the instrument.

The results presented in this paper were made to verify the indications of the above analyser by comparison with those obtained by gas chromatography. The biogas samples for analysis were placed in special bags made of Tedlar® designed for collection of gas samples, produced by SKC, of 1 dm^3 in capacity (Fig. 3) [8].

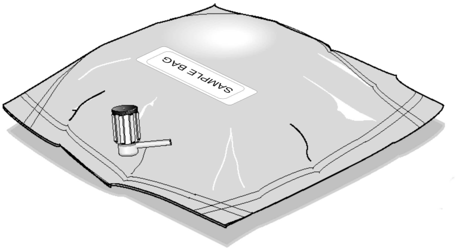

Fig. 3. A bag for collection of gas samples, the version with one valve

Each bag was filled with biogas with the help of a specially constructed kit enabling careful washing of the bag with the sample. Following the recommendations the process of washing the bag with the sample was repeated 10 times before the final filling. The sample collected was analysed on a gas chromatograph HEWLLET-PACKARD model 5890 series II equipped with a *thermal conductivity detector* (TCD). The retention times and peak areas were calculated by the program controlling the work of the chromatograph HP 3365 Series II ChemStation.

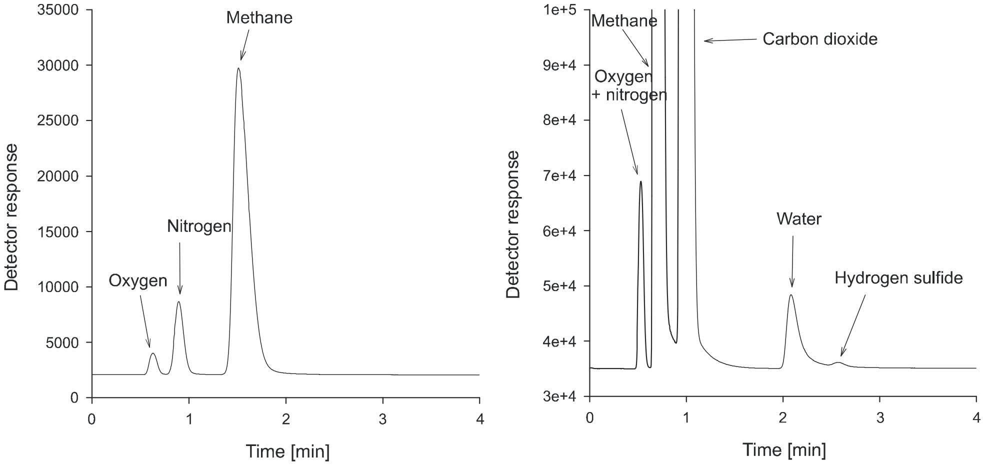

Fig. 4. Exemplary chromatograms revealing the sequence of elution of the components on the columns used. The chromatogram on the left was obtained on the column filled with molecular sieves 5A, while that on the right on the column filled with HayeSep Q polymer

The sample of 0.3 cm^3 in volume was injected on the column with a gas-tight syringe. The components analysed were separated on two columns: one of 2.5 m in length and 1/8 inch in diameter filled with HayeSep Q polymer and the other of 1.5 m in length and 1/8 inch in diameter filled with molecular sieves 5A. The first column was used to determine the content of air, methane, carbon dioxide - in the low sensitivity mode and steam and hydrogen sulphide - in the high sensitivity mode. The second column was used to determine the content of oxygen and nitrogen - in the high sensitivity mode. The separation was performed in isothermal conditions, at 75°C for the column filled with molecular sieves and at 80°C for the column filled with polymer. Exemplary chromatograms of the biogas analysed are presented in Figure 4.

Results and discussion

The monitoring of biogas composition was performed at the Central Wastewater Purification Plant for Poznan, in Kozieglowy. Biogas was collected at a few sites to get the information on its composition in the process of formation and later its use as energy source. The collection sites were placed at six fermentation chambers, at the desulphurisation chamber and at energy generators.

The lack of data for steam and nitrogen among the determinations by GA2000 is a consequence of impossibility of their determination by the analyser of this type. Similarly it was impossible to determine the content of hydrogen sulphide on the gas chromatograph as the LOD of the analytical system (HayeSep Q filled column and TCD detector) was 300 ppm and in the biogas samples studied hydrogen sulphide occurred at lower contents.

Comparison of the results of determinations (Table 3) shows that the difference between the results obtained by the analyser and those obtained by gas chromatography was at a level of 1.0÷1.5% for methane and 0.5÷1.0% for carbon dioxide. These results are much better than 3.0% declared by the producer of the GA2000 analyser. Close agreement between the analyser indications and results of gas chromatography follows from a high quality of the reference standards that were prepared according to PEH (*close manufacturing tolerance*) to maintain the declared composition to the accuracy of 0.1% for methane and carbon dioxide and 1 ppm for hydrogen sulphide. The use of reference mixtures of the highest quality ensured the close agreement of the results despite the fact that we used reference mixtures from two producers in the period of the study (2008-2010). The use of two mixtures was necessary as the stability of certified material of this type reaches only 2 years. The contents of CH_4 and CO_2 indicated by the analyser were usually slightly overestimated with respect to chromatographic determinations, while the content of O_2 was always a bit lower than indicated by GC. The differences follow from the specific method of sample collection for GC analysis, which makes it impossible to totally remove air from the bags during the filling.

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Table 3

Comparison of the biogas composition determined by GA2000 analyser and gas chromatography

Sample labelling (date of collection)	**GA2000**				**GC**				
	Component determined[*]								
29.03.2010	**O_2**	**CH_4**	**CO_2**	**H_2S**	**O_2**	**N_2**	**CH_4**	**CO_2**	**H_2O**
Bioreactor 18.1	0.0	60.7	38.3	68	0.1	0.4	58.9	39.3	1.3
Bioreactor 18.2	0.0	61.9	36.8	21	0.2	0.8	60.3	37.8	0.9
Bioreactor 18.3	0.0	62.5	37.1	29	0.1	0.4	61.1	37.7	0.7
Bioreactor 18.4	0.0	61.9	37.8	69	1.3	5.9	55.2	36.6	1.0
Bioreactor 18.5	0.0	61.9	37.2	15	0.1	0.7	60.2	38.2	0.8
Bioreactor 18.6	0.0	62.4	38.0	44	0.1	0.4	59.3	39.4	0.8
Before desulphurisation chamber	0.0	61.8	37.8	67	0.2	0.5	60.1	38.3	0.9
After desulphurisation chamber	0.0	61.8	37.5	45	0.1	0.6	60.5	38.1	0.7
Before power generator	0.0	61.6	38.2	13	0.2	0.8	59.6	38.6	0.8
05.10.2009									
Bioreactor 18.1	0.1	63.1	36.3	149	0.1	0.4	62.4	36.2	0.9
Bioreactor 18.2	0.2	63.3	36.4	155	0.1	0.4	63.1	35.7	0.7
Bioreactor 18.3	0.4	62.1	35.7	84	0.5	2.8	61.1	34.9	0.7
Bioreactor 18.4	0.2	61.0	34.5	72	1.3	6.0	58.3	33.5	0.9
Bioreactor 18.5	0.3	63.2	35.4	65	0.1	0.6	63.3	35.3	0.7
Bioreactor 18.6	0.3	62.1	34.8	54	0.7	3.3	61.4	33.9	0.7
Before desulphurisation chamber	0.2	64.9	35.0	163	0.3	1.9	62.3	34.9	0.6
After desulphurisation chamber	0.2	64.9	35.0	5	0.2	0.7	63.3	35.2	0.6
Before power generator	0.0	66.6	34.5	278	0.2	0.9	63.1	35.2	0.6
01.07.2009									
Bioreactor 18.1	0.1	60.8	37.9	162	0.1	0.2	60.5	37.9	1.3
Bioreactor 18.2	0.4	52.0	33.7	122	3.2	12.3	50.7	32.5	1.3
Bioreactor 18.3	0.1	61.9	37.6	12	0.1	0.3	61.1	37.2	1.3
Bioreactor 18.4	0.1	62.1	37.3	117	0.1	0.2	61.7	36.6	1.4
Bioreactor 18.5	0.0	61.3	37.2	0	0.3	1.6	59.9	36.8	1.4
Bioreactor 18.6	0.1	62.7	36.4	190	0.1	0.3	62.4	36.0	1.2
Before desulphurisation chamber	0.2	61.3	37.7	163	0.2	0.7	60.6	37.0	1.5
After desulphurisation chamber	0.3	61.1	37.7	30	0.3	1.0	60.3	36.8	1.6
Before power generator	0.5	59.9	37.9	0	0.5	1.8	59.4	36.9	1.4
01.07.2008									
Bioreactor 18.1	0.2	58.9	37.8	86	0.1	0.1	60.4	38.8	0.6
Bioreactor 18.2	0.2	58.9	37.7	97	0.1	0.2	60.3	38.8	0.6
Bioreactor 18.3	0.2	58.1	38.5	61	0.1	0.3	60.4	38.6	0.6
Bioreactor 18.4	0.1	59.9	36.9	71	0.1	0.6	61.3	37.3	0.7
Bioreactor 18.5	0.1	59.4	37.1	26	0.1	0.4	61.1	37.9	0.5
Bioreactor 18.6	0.2	58.6	36.5	26	0.2	1.1	61.3	36.8	0.6
Before desulphurisation chamber	0.0	59.9	37.6	63	0.1	0.3	60.9	37.9	0.8
After desulphurisation chamber	0.0	59.9	37.4	25	0.1	0.3	61.6	37.5	0.5
Before power generator	0.1	59.2	37.8	21	0.2	0.6	60.5	38.1	0.6

[*] concentration of all components except H_2S is given in volume %, the content of H_2S is given in ppm

Comparison of the results of determinations (Table 3) shows that the difference between the results obtained by the analyser and those obtained by gas chromatography was at a level of 1.0÷1.5% for methane and 0.5÷1.0% for carbon dioxide. These results are much better than 3.0% declared by the producer of the GA2000 analyser. Close agreement between the analyser indications and results of gas chromatography follows from a high quality of the reference standards that were prepared according to PEH (*close* *manufacturing tolerance*) to maintain the declared composition to the accuracy of 0.1% for methane and carbon dioxide and 1 ppm for hydrogen sulphide. The use of reference mixtures of the highest quality ensured the close agreement of the results despite the fact that we used reference mixtures from two producers in the period of the study (2008-2010). The use of two mixtures was necessary as the stability of certified material of this type reaches only 2 years. The contents of CH_4 and CO_2 indicated by the analyser were usually slightly overestimated with respect to chromatographic determinations, while the content of O_2 was always a bit lower than indicated by GC. The differences follow from the specific method of sample collection for GC analysis, which makes it impossible to totally remove air from the bags during the filling.

Conclusions

1. The agreement between the GA2000 analyser indications and GC results was at a level of 1.0÷1.5% for methane and 0.5÷1.0% for carbon dioxide, so better than 3.0% declared by the producer.
2. The high quality of the reference mixtures used, prepared according to PEH (*close manufacturing tolerance*) had important effect on the agreement between the GA2000 analyser and GC chromatography data.

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METODY CHROMATOGRAFICZNE, SPEKTROFOTOMETRYCZNE I ELEKTROCHEMICZNE W OZNACZANIU SKŁADU BIOGAZU

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Abstrakt: Biogaz to mieszanina różnych gazów, wśród których dwie trzecie stanowi metan (CH_4), jedną trzecią ditlenek węgla (CO_2). Pozostałe składniki nieorganiczne, organiczne i para wodna występują w biogazie w ilościach śladowych. Aby móc sprawnie kontrolować przebieg procesu fermentacji, należy kontrolować takie parametry, jak: rodzaj oraz ilość doprowadzanych substratów, temperaturę procesu, wartość pH, ilość krótkołańcuchowych kwasów tłuszczowych, stan zapełnienia fermentatora oraz ilość i skład chemiczny otrzymanego gazu. W pracy przedstawiono wyniki badań dotyczących oznaczania składu ilościowego za pomocą popularnego przenośnego analizatora biogazu, jakim jest GA2000, w którym odczyt zawartości metanu i ditlenku węgla odbywa się metodą spektrofotometryczną, natomiast poziomu tlenu i siarkowodoru - elektrochemicznie. Otrzymane wyniki weryfikowano za pomocą chromatografii gazowej.

Słowa kluczowe: biogaz, chromatografia gazowa, analizatory biogazu, weryfikacja pomiarów

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THE EFFECT OF ENVIRONMENTAL FACTORS ON MICROPOLLUTANTS IN SMALL WATER BODIES

WPŁYW CZYNNIKÓW ŚRODOWISKOWYCH NA POZIOMY MIKROZANIECZYSZCZEŃ W WODACH MAŁYCH ZBIORNIKÓW

Abstract: Small water bodies serve a very important function in landscape. Unfortunately, many of them are strongly polluted or are being eliminated. Analyses were conducted on thirteen small water bodies located in the Gen. Dezydery Chlapowski Landscape Park. The water bodies differed in terms of the location in landscape, morphometric parameters (depth, shape, area) as well as aquatic and marshy vegetation. Some of them are typical water bodies of agricultural and forest landscapes, while the others are located in rural areas and in parks. The aim of the conducted investigations was to analyse the level of water pollutants in the water bodies in terms of contents of elements and biogens. Analyses were to explain how environmental variables (dependent, explanatory) influence the distribution of investigated parameters in waters of small water bodies. The analysed parameters included contents of trace elements (Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Ag, Cd, Ba, Tl, Pb as well as too Na, K, Fe, Ca, Mg) and values of pH in waters of thirteen water bodies. Analyses were conducted in the years 2008-2010. The experimental cycle were completed with analyses of ammonia nitrogen, nitrates(III), nitrates(V) and phosphates for waters of all the water bodies. The above-mentioned parameters were subjected to statistical analyses, for which RDA models were prepared taking into consideration dependent and explanatory variables.

Keywords: water body, trace elements, biogenic, RDA model

Introduction

In the last decade increasing attention has been focused on natural resources, which are becoming depleted at a dramatic rate. One of the most important natural raw materials is water, particularly fresh water, which is the primary component in living organisms.

In agriculturally utilised areas water shortage is a major factor with an adverse effect on the functioning of the agricultural ecosystem. Water deficit depends mainly on the distribution and amount of precipitation, as well as water retaining capacity of soil. Water cycle in the agricultural ecosystem is also influenced by the structure of landscape. In areas with a monotonous landscape of fields considerable amounts of water are discharged with

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runoff outside catchments, while in areas with a diverse landscape these water shortages are much smaller.

The Gen. Dezydery Chlapowski Landscape Park is characterised by a varied agricultural landscape. Through cultivation measures connected with the modification of the agricultural landscape in that area a unique system of landscape elements has been formed. Fields are interwoven with numerous tree plantings as well as small watercourses and small water bodies. The latter have a positive effect on water retention by trapping of surface flows during and after intensive precipitation periods [1-4]. Small midfield water bodies are also ascribed an important function in the reduction of surface washings, serving the role of biogeochemical barriers [5-7]. Small water ecosystems located in agricultural areas are also habitats for many, frequently rare species of flora and fauna [8-10], and by harmonising with other elements of the agricultural ecosystems they serve the landscape-forming function [11].

The disappearance of small water bodies may be caused by natural processes occurring in those reservoirs; however, a definitely greater role is attributed to human activity in this process. The phenomenon of the disappearance of many small water bodies has been observed in different regions of Poland. Most small water bodies have been filled in and next managed for agricultural purposes, some became landfill sites, while still others have been subjected to accelerated evolution processes (through systematic release of pollutants) and as a consequence they have changed into terrestrial ecosystems [12].

The aim of the presented studies was to determine contents of trace elements and biogens in waters of the examined water bodies and to verify whether and how environmental factors, ie water reaction, temperature, ecological status (E) [13], location or depth of water bodies, influence changes in the analysed parameters.

Material and methods

Investigations were conducted in the Gen. Dezydery Chlapowski Landscape Park. The object of the study comprised 13 water bodies differing in terms of their location in the landscape, area, shape, shoreline development, aquatic vegetation, type of subsoil, in which they are found. Some small water bodies are typical midfield depressions, some are situated in built-up areas, while two are located in a forest complex (Fig. 1).

Water bodies located in forests

Two water bodies, denoted as nos. 1 and 2, are located in the Rabinsko-Blociszewski Forest Complex (Fig. 1). The first (Fig. 2) small, with an area of approx. 92 m^2, is situated in the south-eastern part of the forest complex, in a small depression among oaks with an admixture of hornbeams and birches. Slightly loamy sands predominate in the upper subsoil horizons. The small water body is characterised by a small maximum depth (0.5 m) and considerable thickness of bottom deposits (in relation to the area of water bodies), originating mainly from falling leaves, accumulating in the water body.

The other water body denoted as no. 2 (Fig. 3) is a man-made hollow, without drainage and area of approx. 885 m^2. It is surrounded mainly by spruces, oaks and larches. A characteristic feature of this water body is its milky colour, while loamy sands are found in the upper subsoil horizons. The subsoil of this hollow comprises primarily mineral deposits and its depth in places is up to 1 m.

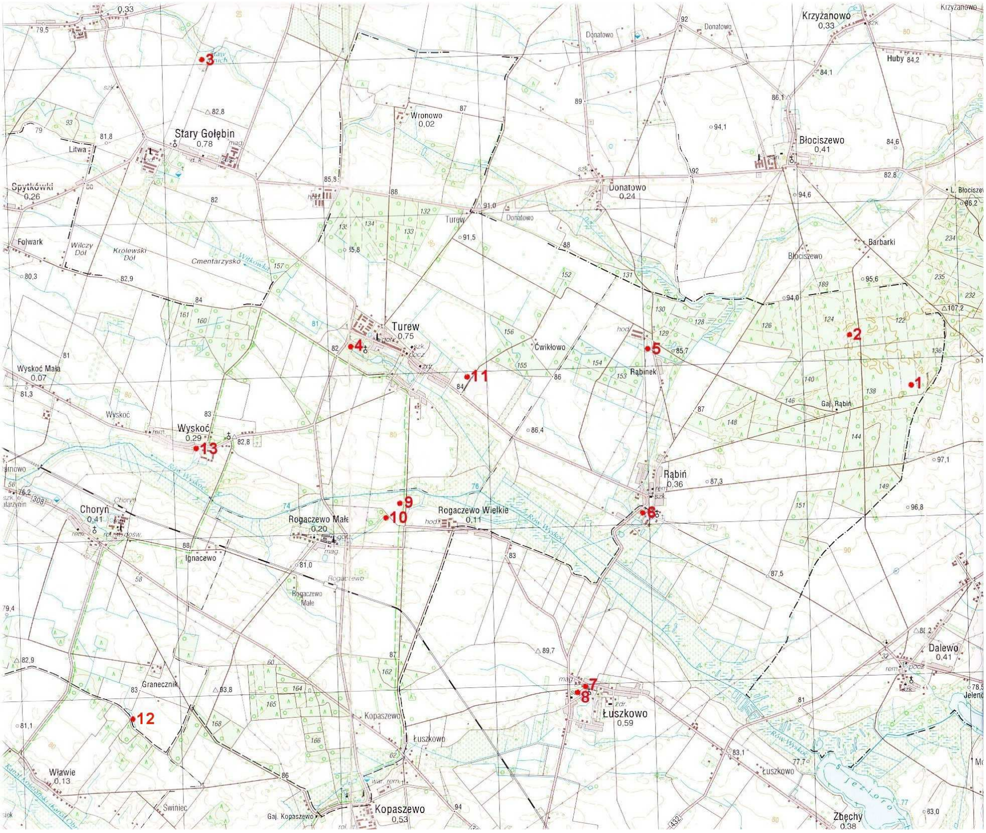

Fig. 1. A location map

Fig. 2. A forest reservoir (1)

Fig. 3. A forest reservoir (2)

Water bodies located in agricultural areas

Analysed water bodies located in agricultural areas were denoted with nos. 3, 5, 9, 10, 11 and 12. Water body no. 3, (Fig. 4) covering 2538 m^2, is situated north of a village of Golebin Stary. It is surrounded predominantly by fields and meadows used as grassland, and mainly willows, lilacs and hawthorns found within the shoreline. The maximum depth of the water body is 1.5 m, whereas bottom deposits are mainly of organic origin and are 30 cm deep.

Fig. 4. An agricultural reservoir (3)

The most diverse surroundings are found around water body no. 5 (Fig. 5). On the eastern side the water body borders with a tree planting composed primarily of locusts, birches and oaks, behind which a hard-surfaced road is located. The other components of the surroundings of this water body comprise mainly fields and single trees (birches, pines and oaks). On the eastern side along the dried ditch the area is covered by a large phytocenosis of nettle, which may indicate the runoff of nitrates from fields. The water body occupies an area of 1668 m^2 and the upper subsoil layer at the water body consists of loose sands.

Fig. 5. An agricultural reservoir (5)

Fig. 6. An agricultural reservoir (9)

Water body no. 9 (Fig. 6) was recreated in 1995. In the course of its construction on the northern, western and southern side shores were formed as steep escarpments, while the eastern shore remained flat. The water body is surrounded by fields on three sides, which influences the process of eutrophication of this water body. This water body is characterised by a shallow deposition of bottom sediments (10 cm) and an area of 1929 m^2. The upper soil horizon in areas adjacent to the water body is composed mainly of loamy sands.

Water body no. 10 (Fig. 7) is situated at a small distance from water body no. 9. It is located east of the village of Rogaczewo Male, in a natural depression with a depth of max 1 m. From the north-west the water body is planted with trees with locusts predominating, while it is separated with a narrow belt of meadows from arable fields. The water body is 919 m^2 in area and the bottom is filled with organic deposits of considerable thickness. Adjacent areas in terms of grain size composition consist mainly of loose sands.

Fig. 7. An agricultural reservoir (10)

Fig. 8. An agricultural reservoir (11)

Water body no. 11 (Fig. 8) is located within the boundaries of the village of Turew. It is one of the largest analysed water bodies. It is 3026 m^2 in area and the bowl of the pond is mostly overgrown with reed rushes. Willows and in smaller numbers also hawthorns and locusts grow within a close distance from the shore of the water body. Areas adjacent comprise fields separated by a meadow from the south. On the western side a hard-surfaced road is located. Among the analysed water bodies water body no. 12 (Fig. 9) stretches farthest to the south-west. It is located approx. 1 km south of the village of Granecznik. In the 1960's this water body retained greater amounts of water and was used by the population of the neighbouring villages for recreation purposes. At present it is shallow and it is gradually disappearing. In 2009 in the summer-autumn period there was no water in this reservoir. It is a typical midfield water body surrounded by fields on all sides, with abundant rush vegetation overgrowing almost the entire surface of the water body.

Fig. 9. An agricultural reservoir (12)

Water bodies located in built-up areas

Water bodies denoted as nos. 4, 6, 7, 8 and 13 are located in built-up areas. Water body no. 4 (Fig. 10) is a pond situated in a palace park at Turew.

Fig. 10. A reservoir in a built-up area (4)

It is a flow-through water body with an area of 1344 m^2. The water body is surrounded mainly by park tree plantings, with the predominance of oaks, alders, maples, but also *Ailanthus altissima* (the tree of heaven). Soil at the water body is composed mainly of sandy loam.

In the village of Rabin analyses were conducted on water body no. 6 (Fig. 11). It is on two sides surrounded by an asphalt road, while on the south it is a hard-surfaced road. The adjacent areas comprise mainly meadows. In the narrow belt at the water body we may find trees characteristic of rural areas, ie linden and apple trees, as well as those typical of areas located at water reservoirs, ie willows. The water body occupies an area of 1992 m^2 and the bottom is covered by deposits of organic matter.

Fig. 11. A reservoir in a built-up area (6)

Fig. 12. A reservoir in a built-up area (7)

Water bodies nos. 7 and 8 (Figs 12 and 13) are situated in the village of Luszkowo. They are small drainless depressions with an area of 358 and 432 m^2, respectively. Around the water bodies predominant species are poplars, willows and locusts. In 2010 all the trees at water body no. 7 were felled. Both depressions are typical rural water bodies.

Fig. 13. A reservoir in a built-up area (8)

Water body no. 13 (Fig. 14) is located in the village of Wyskoc, it is surrounded by an asphalt road from the north, buildings from the south, while from the west it is surrounded by a brick wall. The trees around the water body are mainly lindens, maples and birches and the area of the reservoir is 1173 m^2. The upper soil layer at the water body is composed predominantly of loamy sands.

Fig. 14. A reservoir in a built-up area (13)

Analyses covering 2 complete experimental cycles were conducted in the years 2008-2010. In waters of the thirteen water bodies analyses concerned contents of trace elements (Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Ag, Cd, Ba, Tl, Pb as well as Na, K, Fe, Ca, Mg), and also pH values.

In order to provide a more comprehensive characteristic of analyzed objects analyses also focused on ammonia nitrogen, nitrates(III), nitrates(V) and phosphates for waters of all water bodies.

Collection and preparation of samples for analyses

The examined material came from thirteen water bodies located in the Gen. Dezydery Chlapowski Landscape Park, differing in terms of morphometric characteristics and their location in the landscape.

Collection of water samples was performed according to the standard PN-74/C-04620/02 [14]. Samples were collected at a distance of approx. 1 m from the shore of the water bodies at a depth from 20 to 50 cm. Water was collected to Nalgene bottles of 125 cm^3, made from *high density polyethylene* (HDPE). In order to avoid contamination of the material, bottles were washed with distilled water and next filled with water from the water bodies. During samplings care was taken to prevent solid pollutants (fractions of deposits or fragments of plant organs). Next water samples were acidified on site using 65% nitric acid at 2 cm^3 (for contents of trace elements), while water samples for contents of nitrates(V), nitrates(III), ammonia nitrogen and orthophosphates were transported to the laboratory on the sampling day and filtered. Preparatory work at the laboratory consisted in filtering of water samples through Peel Corner Milipore filters of 47 mm in diameter (pore diameter of 0.45 μm). Such prepared material was ready for chemical analysis.

Methods used in the analysis of elements

Elements were analysed using the following analytical methods:

- *Flame Atomic Absorption Spectrometry* (F-AAS) - Ca, Mg, Fe (Table 1)

Table 1

Values of optimisation parameters in F-AAS

Optimisation parameters	**Elements**		
	Ca	**Mg**	**Fe**
lamp current [mA]	10	6	30
wavelength [nm]	422.67	285.21	248.33
gap [nm]	2.7/0.6	2.7/1.05	1.8/1.35
flow of oxidising gas (air) [dm^3/m]	10.00	10.00	10.00
flow of flammable gas (acetylene) [dm^3/m]	2.70	2.50	2.50
integration time [s]	3.0	3.0	3.0
reading time [s]	5.0	5.0	5.0

– *Atomic Emission Spectrometry* (AES) - Na, K (Table 2)

Table 2

Values of optimisation parameters in AES

Optimisation parameters	**Elements**	
	Na	**K**
lamp current [mA]	-	-
wavelength [nm]	589.00	766.49
gap [nm]	1.8/0.6	1.8/0.6
flow of oxidising gas (air) [dm^3/m]	10.00	10.00
flow of flammable gas (acetylene) [dm^3/m]	2.5	2.5
integration time [s]	3.0	3.0
reading time [s]	5	5

– *Inductively Coupled Plasma Mass Spectrometry* (ICP-MS) - Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Ag, Cd, Ba, Tl, Pb (Table 3)

Table 3

Parameters for an ELAN DRC II apparatus, PerkinElmer, Sciex, Canada

Mass analyser	Quadrupole
Sprayer	Meinhard concentric
Cloud chamber	Cyclone quartz chamber kwarcowa
Power of plasma generator [W]	1200.00
Flow of sprayer gas [dm^3/min]	0.95
Flow of auxiliary gas [dm^3/min]	1.20
Voltage at lenses [V]	6.00
Scanning mode	Pulse
Internal standard	^{45}Sc, ^{89}Y, ^{159}Tb

Analyses (F-AAS) and (AES) were performed at an AAS AAnalyst 200 spectrometer, while (ICP-MS) at an ICP-MS ELAN DRC II spectrometer.

The following parameters were determined using colorimetric methods:

- ammonia nitrogen - by colorimetry with Nessler reagent,
- nitrates(III) - by colorimetry with sulfanilic acid and naphthylamine,
- nitrates(V) - by colorimetry with sodium salicylate,
- orthophosphates - by the molybdate method.

In all colorimetric methods the blank test performed as the primary standard was used as reference.

Values of pH and water temperature were measured with a watertight pH-meter CP-411 with a glass electrode type EPS-1.

Results

Mean contents of elements and pH values in waters of examined water bodies

By analysing all levels in individual water bodies, the quantitative series was prepared for the elements found in the waters of reservoirs in the Gen. Dezydery Chlapowski Landscape Park. Tables 4 to 6 present mean contents of examined analytes detected in each of the thirteen water bodies.

Analysed elements formed the following series:

- Na > K > Ca > Mg > Fe > Mn (Table 4),
- Sr > Al > Ba > Zn > Li > Cu ≥ Ni ≥ As (Table 5),
- V ≥ Cr ≥ Pb > Co ≥ Cd > Ag > Se ≥ Tl (Table 6).

The elements found as predominant in the waters of most water bodies were Na, K and Ca, which is understandable, since next to phosphorus, potassium and sodium they are main elements contained in fertilisers. Together with calcium they serve many important functions in living organisms, both animals and plants. Definitely highest contents of sodium and potassium were found in water bodies nos. 6, 7 and 8 (each of the three water bodies is located in a built-up area), which suggests that the elevated contents of these elements may be indirectly affected by human activity.

Slight amounts of magnesium and calcium in comparison with the other water bodies (Table 4) were found in water bodies nos. 1 and 2 (located in a forested area), which indicates that water in those reservoirs is characterised by a definitely lower hardness and lower pH values (ranging from 4.91 to 5.78 - Table 7). In turn, the acid reaction of water could have influenced the elevated values of other elements such as Fe, Al or Zn.

Iron concentration ranged from 0.089 mg dm^{-3} in water body no. 12 to 2.552 mg dm^{-3} in water body no. 1. The content of manganese in the water of water bodies was much more uniform and ranged from 0.099 mg dm^{-3} in water body no. 3 to 0.982 mg dm^{-3} in water body no. 12.

Table 4

Mean contents of elements (Na, K, Ca, Mg, Fe and Mn) in waters
of analysed water bodies in the years 2008-2010

	[mg dm^{-3}]					
Water body	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**
no. 1	19.830	44.280	2.755	1.039	2.552	0.323
no. 2	11.980	20.438	1.778	0.638	1.751	0.076
no. 3	57.052	30.170	49.980	11.204	0.522	0.099
no. 4	72.638	32.926	90.900	11.902	0.758	0.267
no. 5	42.108	82.932	33.575	4.821	0.491	0.115
no. 6	142.822	173.282	68.871	10.856	0.416	0.455
no. 7	177.555	183.838	28.401	8.205	0.497	0.570
no. 8	219.406	153.722	23.067	9.324	0.461	0.534
no. 9	79.194	40.648	77.147	9.422	0.338	0.274
no. 10	82.994	26.728	84.560	9.728	0.299	0.188
no. 11	89.702	74.422	82.824	11.215	0.340	0.588
no. 12	86.090	51.560	81.233	13.600	0.089	0.982
no. 13	99.962	67.080	44.058	4.729	0.161	0.196
MEAN	**90.872**	**75.540**	**51.473**	**8.206**	**0.667**	**0.359**

Strontium is an element found in waters of the water bodies at levels from 8.590 to 528.600 μg dm^{-3} and they values were similar to those of manganese (Table 5), although its biogeochemical properties are similar to those of calcium. Very high contents of aluminium were recorded in water bodies nos. 1, 2 and 5, with values ranging from 253.149 to 1063.819 μg dm^{-3}. Such very high concentrations were probably influenced by the reaction of water and the slight content of ions of magnesium and calcium (in case of water bodies nos. 1 and 2).

Barium in highest amounts (289.943 μg dm^{-3}) was found in waters of water body no. 3, where its values exceeded even 7 times the contents recorded in waters of the other water bodies. In agricultural areas the highest amounts of barium originate mainly from the combustion of liquid fuels and coal. Zinc, lithium, copper, nickel and arsenic were found at much lower contents in waters of the reservoirs water bodies. The highest zinc content was detected in waters of forest water bodies, while that of lithium - in water bodies located in agricultural areas located in villages or near them (Table 5).

Table 5

Mean contents of elements (Sr, Al, Ba, Zn, Li, Cu, Ni and As) in waters of analysed water bodies in the years 2008-2010

	[μg dm^{-3}]							
Water body	**Sr**	**Al**	**Ba**	**Zn**	**Li**	**Cu**	**Ni**	**As**
no. 1	13.578	389.187	77.028	21.971	1.080	7.304	2.547	1.593
no. 2	8.590	1063.819	30.871	21.713	1.228	7.053	2.887	0.877
no. 3	266.657	42.111	289.943	7.810	10.711	3.926	1.709	1.285
no. 4	361.086	11.377	97.643	5.887	7.690	2.853	3.639	2.520
no. 5	225.400	253.149	53.657	14.702	0.780	7.011	3.081	2.067
no. 6	375.714	12.913	85.186	15.079	17.843	2.348	3.389	4.493
no. 7	528.600	15.592	60.520	12.180	8.502	3.807	6.770	4.288
no. 8	473.000	15.606	56.128	13.530	6.584	4.848	4.123	3.878
no. 9	392.143	10.591	78.543	5.973	6.043	2.712	3.514	2.687
no. 10	432.286	11.933	75.386	5.211	4.396	2.158	3.215	2.579
no. 11	353.857	8.871	77.600	4.601	1.511	1.840	2.374	2.668
no. 12	530.000	14.390	40.825	6.687	3.010	2.490	5.091	5.707
no. 13	207.971	27.503	52.683	8.046	11.333	3.080	3.672	4.103
MEAN	**320.683**	**144.388**	**82.770**	**11.030**	**6.209**	**3.956**	**3.539**	**2.980**

Table 6

Mean contents of elements (V, Cr, Pb, Co, Cd, Ag, Se and Tl) in waters of analysed water bodies in the years 2008-2010 (n.d. - not detected)

	[μg dm^{-3}]							
Water body	**V**	**Cr**	**Pb**	**Co**	**Cd**	**Ag**	**Se**	**Tl**
no. 1	2.861	2.337	5.986	0.757	0.249	0.054	0.003	0.054
no. 2	2.833	2.973	5.771	0.894	0.255	0.052	n.d.	0.045
no. 3	0.449	1.096	0.498	0.066	0.202	0.027	n.d.	0.017
no. 4	0.826	1.540	0.719	0.142	0.236	0.583	0.019	0.022
no. 5	2.682	2.813	1.713	0.291	0.257	0.058	0.005	0.029
no. 6	1.049	5.196	0.924	0.222	0.232	0.084	0.251	0.032
no. 7	2.560	1.138	1.077	0.430	0.284	0.031	n.d.	0.030
no. 8	2.832	1.795	0.830	0.328	0.272	0.065	n.d.	0.027
no. 9	1.480	1.408	0.528	0.124	0.226	0.466	n.d.	0.022
no. 10	1.370	0.863	0.999	0.176	0.245	0.374	n.d.	0.024
no. 11	1.387	0.901	0.647	0.130	0.280	0.053	0.128	0.026
no. 12	2.710	1.624	0.466	0.270	0.370	0.117	n.d.	0.038
no. 13	2.194	0.837	0.808	0.165	0.201	0.053	n.d.	0.016
MEAN	**1.941**	**1.886**	**1.613**	**0.307**	**0.255**	**0.155**	**0.031**	**0.029**

A similar mean concentration in all the water bodies, but different fluctuations between individual water bodies were found for vanadium, chromium and lead (Table 6). Contents of these elements ranged from 0.466 μg dm^{-3} for lead contained in water of water body no. 12 up to 5.986 μg dm^{-3} for lead in water of water body no. 1. Among these 3 elements the greatest changes in contents in waters within the analysed water bodies were observed for lead, while they were smallest for vanadium. Very small values of around tens of μg dm^{-3} were recorded for cobalt, cadmium and silver, while they were slight at around of hundreds of μg dm^{-3} for selenium and thalium, with selenium not detected in waters of most reservoirs (Table 6).

Water reaction is a very important parameter influencing forms of these elements in waters. At low pH values mainly soluble forms predominate, while at higher values metals are precipitated from waters and deposited in sediments. Mean values of pH recorded in waters of water bodies are presented in Table 7.

Table 7

Mean values of pH for waters in the analysed water bodies measured in the years 2008-2010

Water body	**pH value**	**Water body**	**pH value**	**Water body**	**pH value**
no. 1	4.91÷5.78	no. 6	7.36÷8.63	no. 10	6.81÷7.43
no. 2	4.83÷5.63	no. 7	6.23÷6.86	no. 11	6.90÷7.83
no. 3	6.23÷6.87	no. 8	7.52÷8.01	no. 12	7.41÷7.77
no. 4	6.87÷7.27	no. 9	6.70÷7.21	no. 13	8.2÷8.74
no. 5	5.03÷6.11				

Among the analysed water bodies there were water bodies containing both water of acid reaction in water bodies nos. 1, 2 and 5, and slightly alkaline in water bodies nos. 6, 8 and 13. Water reaction influenced contents of metals in waters. At low pH values in water bodies nos. 1, 2 and 5 elevated levels were recorded for Fe, Zn, and particularly Al.

Contents of forms of phosphorus and nitrogen in waters of water bodies

Nitrates(V) and phosphates influence the degree of overgrowing of water bodies and the process of eutrophication.

The highest values of nitrate nitrogen were recorded in water bodies no. 4 (10.34 mg dm^{-3}), no. 9 (6.82 mg dm^{-3}) and no. 10 (5.77 mg dm^{-3}) (Table 8) and these values exceeded all admissible limits [15]. Such high contents could have been caused by leaching of nitrogen compounds originating mainly from fertilisers from fields located nearby.

High values were recorded in case of ammonia nitrogen, which main sources were urea-based fertilisers and animal waste. The highest pollution with this element was observed in water bodies nos. 1, 6 and 7.

Phosphates were accumulated in highest amounts in waters of reservoirs nos. 6, 7, 8, 11 and 13, with the values ranging from 2.202 to 6.824 mg dm^{-3} (Table 8). Such high values could have been influenced by sewage discharged to the water bodies, since all these water bodies are located in villages or in the vicinity of buildings.

Moreover, values considerably exceeding admissible limits were also found for total phosphorus, with the highest levels recorded for water bodies nos. 6, 7 and 8, at up to 2.23 mg dm^{-1}.

Table 8

Contents of ammonia nitrogen, nitrate(III) nitrogen, nitrate(V) nitrogen as well as total phosphorus and phosphates in waters of reservoirs on 05.2010 (n.d. - not detected)

Water body	$N\text{-}NH_4$	$N\text{-}NO_2$	$N\text{-}NO_3$	$P\text{-}PO_4$	P
	[$mgNH_4\ dm^{-3}$]	[$mgNO_2\ dm^{-3}$]	[$mgNO_3\ dm^{-3}$]	[$mgPO_4\ dm^{-3}$]	[$mgP\ dm^{-3}$]
no. 1	7.106	n.d.	0.98	0.803	0.262
no. 2	1.500	n.d.	0.71	0.146	0.048
no. 3	0.702	n.d.	0.56	0.071	0.023
no. 4	0.535	0.022	10.34	0.077	0.025
no. 5	1.353	n.d.	1.62	0.262	0.086
no. 6	2.539	n.d.	0.77	6.824	2.23
no. 7	2.338	n.d.	0.81	3.919	1.281
no. 8	1.486	n.d.	0.66	2.297	0.751
no. 9	1.143	0.051	6.28	0.098	0.032
no. 10	0.991	0.031	5.77	0.389	0.127
no. 11	1.040	n.d.	1.33	3.156	1.031
no. 12	1.045	0.008	1.53	0.082	0.027
no. 13	0.731	n.d.	0.59	2.202	0.72

Statistical analysis of results

Statistical analysis concerned the occurrence of metals in waters and environmental factors, ie reaction of water, temperature, ecological status (E), location and depth.

For the purpose of statistical analysis of the results the CANOCO package was used, applying three components of this package, ie WCanoImp, Canoco 4.5 for Windows and CanoDraw for Windows. This program has huge potential for the analysis of heterogenic numerical sets.

In this paper ordinance techniques were used, ordering samples along the gradient represented both by the axis of ordinates and the axis of abscissae. In order to verify which of the techniques is most suitable for the analysed set of data the *Correspondence Analysis* (CA) was performed. Such a procedure was to identify the character of the structure of the analysed set on the basis of the length of the gradient (linear or unimodal) [16].

The linear model is found when the share of dependent variables (*elements*) in samples decreases or increases in proportion to the size of explanatory variables (*environmental factors*). The unimodal model should be applied when elements are found in a specific spectrum of environmental variables, which is most frequently described by the Gaussian curve. The *Principal Component Analysis* (PCA) among indirect ordinance techniques or *Redundancy Analysis* (RDA) (a canonical form of PCA) among direct ordinance techniques are used at gradient length < 3, whereas at gradient length exceeding 3 we use CA, DCA (*Detrended Correspondence Analysis*) as a technique of indirect ordinance and CCA (*Canonical Correspondence Analysis*), as well as DCCA (*Detrended Canonical Correspondence Analysis*) among direct ordinance techniques.

Correspondence Analysis (CA) showed that for the analysed set the length of gradient is 1.21 (linear distribution), thus in this study PCA and RDA could be applied, of which the latter was selected.

Redundancy Analysis (RDA) was applied to evaluate the dependencies of individual elements in relation to environmental variables and between one another. The group of explanatory variables (environmental factors) included pH, water temperature, ecological status (E), location of a water body and its depth. Moreover, all the thirteen water bodies were compared in terms of the occurrence of elements in waters and the calculated ecological status (E). In the comparative analysis the dates of analyses in the annual cycle were also taken into consideration.

The final stage of statistical analysis was to apply the Monte Carlo permutation test in order to determine the threshold significance level and to verify whether it does not exceed $p = 0.05$. If value p is greater than 0.05, the zero hypothesis, that the observed effect is accidental, may not be rejected.

As it was shown by the analysis below (Fig. 15), the elements with a similar level of variation in concentrations, which were characterized by a high positive correlation included cobalt, lead, iron and copper (sufficiently long vectors and slight angle of flare between these vectors). It is evident that some of the analysed elements could be arranged in pairs (Ag and Ba, Sr and Li, K and Mn as well as Fe and Cu). Such a situation indicates similarity of elements in terms of changes in concentrations in waters taking into consideration the year of study, date in the annual cycle as well as the location of all the thirteen water bodies. A marked negative correlation was found between lead, cobalt and iron on the one hand and strontium and lithium, as it is indicated by the orientation of vectors. These two groups of elements differed considerably in terms of fluctuations in concentrations. When lead, cobalt and iron were characterised by upward trends, the overall trend for the concentration of strontium and lithium in waters was different.

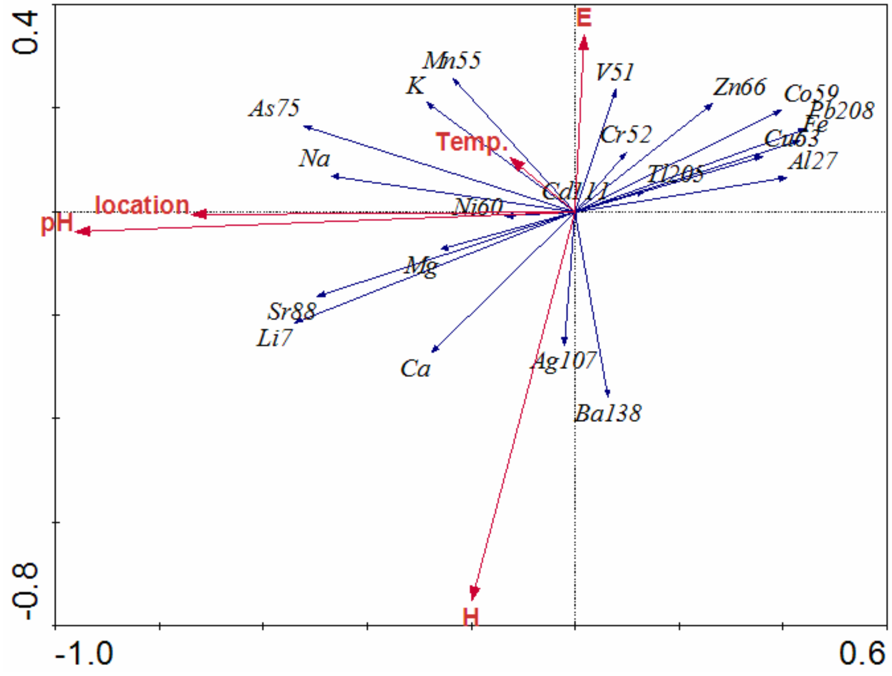

Fig. 15. The RDA model (n = 86) - dependencies between elements in waters of analysed water bodies and environmental variables: E - ecological status, H - depth of water body, pH - reaction of water in a water body, location - location of the water body, Temp. - temperature of water in a water body ($p < 0.05$)

A highly evident negative correlation was found between the reaction of water and contents of certain elements. At low pH values the contents of such elements as aluminium, copper, iron, lead, cobalt or zinc increased.

The slight vector of temperature indicates a small effect of this factor on the other variables. In contrast, a markedly negative correlation was observed between the depth of water bodies and vanadium. Waters of very shallow water bodies contained higher amounts of this element.

Location turned out to be a factor determining the content of specific elements in waters. The most similar water bodies in terms of metal concentrations in waters were water bodies located in the vicinity of fields and the park reservoir. Elements were divided into two distinct groups, correlated with the location (Fig. 16). Mainly Fe, Al, Pb, Co and Zn predominated in waters of forest water bodies. For waters in the water bodies located in built-up areas the characteristic feature was the presence of K, Na and Li. In contrast, no characteristic elements were found for water in the midfield and park water bodies and Ba, Ca and Mg turned out to be the only elements with slight positive correlations. Moreover, a negative correlation was shown between water in the forest water bodies and contents of strontium. In waters of the forest water bodies this element was detected in much smaller amounts in comparison with waters from the other water bodies.

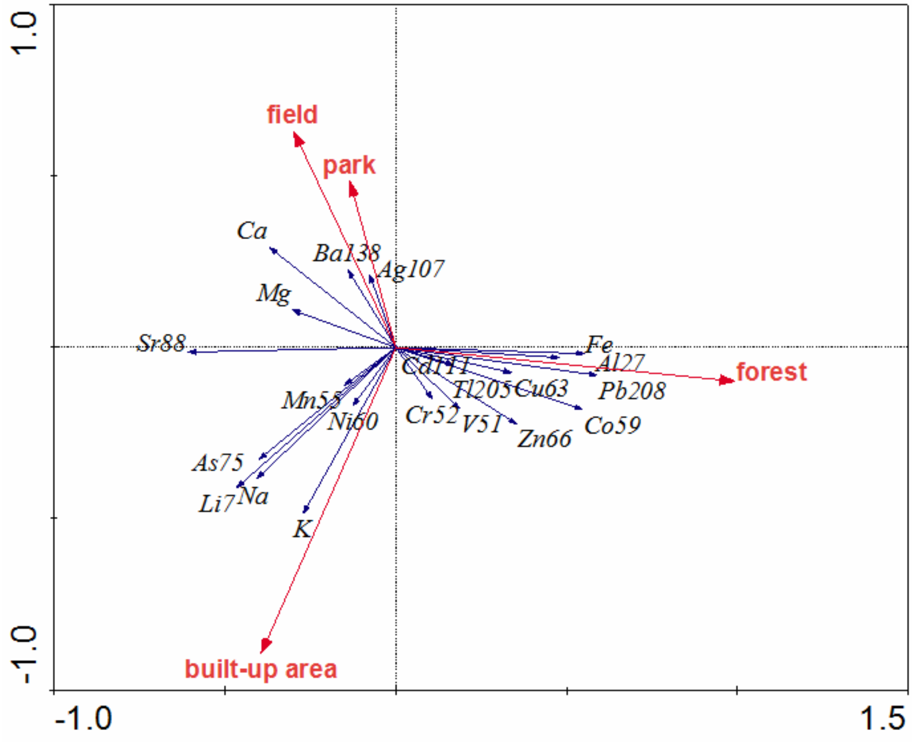

Fig. 16. The RDA model (n = 86) - dependencies between elements in waters and location of the analysed water bodies ($p < 0.05$)

When comparing the analysed water bodies in terms of the date of analysis taking into consideration dependent and explanatory variables, which is presented below (Fig. 17), the degree of correlation between water bodies may be determined in relation to the dates of analysis. In the graph the first number refers to the number of the water body, while the second, separated with a dot, the date of analysis (1 - 07.2008; 2 - 10.2008; 3 - 04.2009; 4 - 07.2009; 5 - 09.2009; 6 - 11.2009; 7 - 05.2010). The lowest variation was found in the analysed parameters in term of the dates of analysis for water bodies nos. 3, 8, 9, 10 and 12. In contrast, the highest variation was observed for water bodies nos. 1, 2, 7, 11 and 13, for which the date of analysis played a much more important role in the variation of the parameters in waters than it was for the others. In the graph water bodies nos. 1, 2, 5, 8, 12 and 13 are distinct, as for them the dates of analysis are not correlated with dates for the other water bodies, which means that time fluctuations of variables are typical solely of these water bodies.

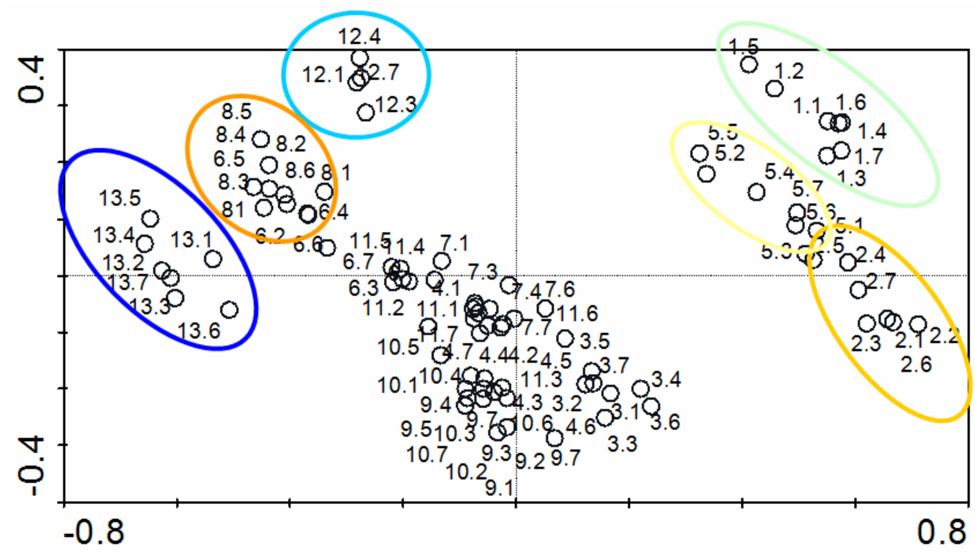

Fig. 17. The RDA model (n = 86) - dependencies between water bodies and dates of analysis in the annual cycle ($p < 0.05$)

Taking into consideration both dependent parameters (analysed elements in waters) and explanatory parameters (pH, value E, temperature, depth, location), but also the co-variate (the date of analysis), the RDA model presented below was prepared (Fig. 18). Marked similarities may be observed in water bodies nos. 1 and 2, which are forest water bodies, but which are also characterised by similar fluctuations of the analysed parameters. Strong similarities were also observed in terms of all the analysed variables recorded for water bodies nos. 7, 8 and 11 as well as nos. 4, 9 and 10. In contrast, water bodies no. 5 and 12 turned out to be completely different in terms of the concentrations of elements in waters, values of E, depth, temperature and fluctuations in those parameters in the annual cycle. They not only differed from the others, but first of all constituted a large difference between these water bodies.

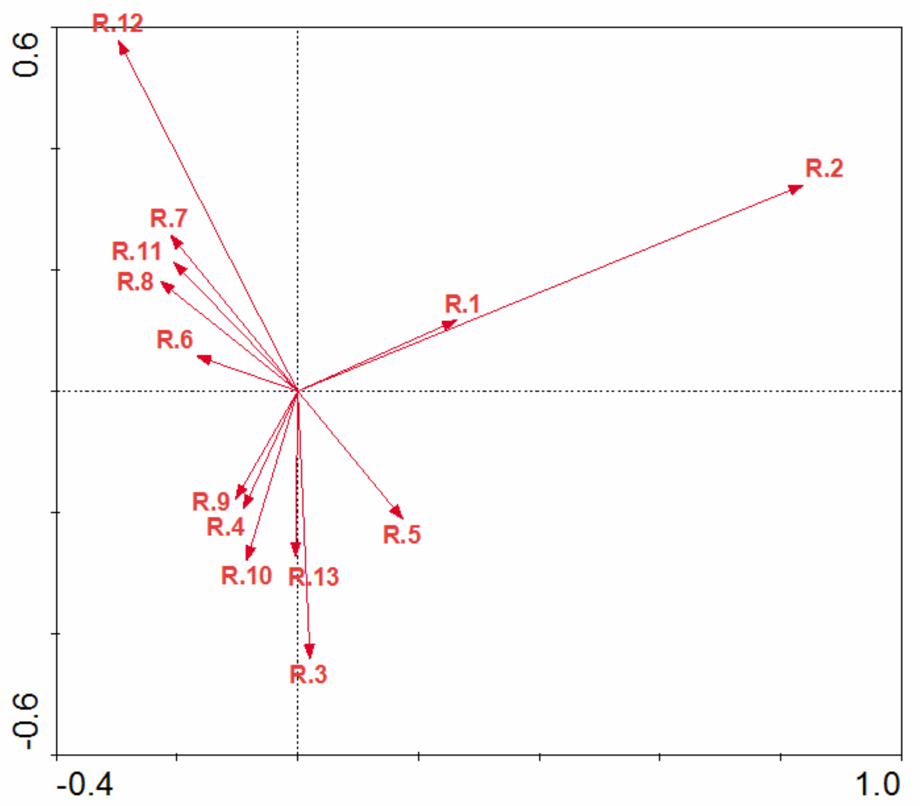

Fig. 18. The RDA model (n = 86) - similarities between water bodies in terms of contents of elements in waters and environmental variables ($p < 0.05$)

Discussion

In the Gen. Dezydery Chlapowski Landscape Park studies concerning contents of heavy metals in waters of water bodies were conducted by Szpakowska et al in 1997 [16]. The objects of analyses comprised 2 midfield ponds differing in their genesis, one being a natural water body and the other a man-made reservoir. Mean contents of ionic forms of heavy metals in waters of the natural water body amounted to 26.4 μg dm^{-3} for Zn, 0.12 μg dm^{-3} for Cd and 4.6 μg dm^{-3} for Pb. In turn, in waters of the man-made reservoir higher contents were recorded amounting to 36.5, 0.3 and 5.7 μg dm^{-3} for Zn, Cd and Pb, respectively. They were higher levels in comparison with the results recorded in this study (higher in case of contents of Zn and Pb and comparable in relation to Cd) (Tables 5 and 6). Lower contents of the first two elements observed in waters of the water bodies in the years 2008-2010 may indicate a reduction of pollution with these heavy metals in the ecosystems in relation to the late 1990's.

In waters of three water bodies in the Gen. Dezydery Chlapowski Landscape Park (which corresponded to reservoirs nos. 3, 9 and 10) studies were conducted in the years

2003-2004 by Arczynska-Chudy on the variation in the contents of ammonia nitrogen, nitrates(V) and phosphates [17]. The recorded concentration of ammonia nitrogen was highest in September 2003 for water body no. 9 (5.04 mg dm^{-3}) and it considerably exceeded the amount of ammonia nitrogen in May 2010 (Table 8). Moreover, a considerable alarming increase was found in the content of nitrate(V) nitrogen, which concentration in the years 2003-2004 ranged from 0.02 to 2.2 mg dm^{-3}, while in April 2010 it was from 0.56 mg dm^{-3} for water body no. 3 to 6.28 mg dm^{-3} for water body no. 9. Also higher contents were recorded for phosphate phosphorus. In the years 2003-2004 the range of phosphate phosphorus contents ranged from 0.004 mg dm^{-3} in July 2004 for water body no. 3 to 0.196 mg dm^{-3} in April 2003 for the same water body. In April 2010 the contents of phosphates amounted to 0.077 mg dm^{-3} in water from water body no. 3, 0.098 mg dm^{-3} in water from water body no. 9 and 0.389 mg dm^{-3} for water from water body no. 10. The increase in the contents of nitrates(V) and phosphates in waters of the water bodies may contribute to the progressing process of eutrophication.

Very high contents of heavy metals were recorded in the three lakes of the Przemecki Landscape Park, located in the area of a village of Boszkowo situated 60 km from Poznan. Lakes Boszkowo and Wielkie are surrounded by pastures, meadows and fields, being situated in an agricultural area. Lake Dominickie (344 ha) is definitely the largest reservoir and it is surrounded by dense developments of holiday homes located in a pine forest. Studies were conducted in the late 1990's [18] and showed very high contents of Zn, amounting to as much as 6450 μg dm^{-3}. In comparison with the results recorded for water from the water bodies located in the Gen. Dezydery Chlapowski Landscape Park (mean Zn content of 11.03 μg dm^{-3}) those contents were 580 times higher. Lakes in the area of Boszkowo were also characterised by higher levels of nickel (9.0÷11.2 μg dm^{-3}), chromium (5.69÷7.25 μg dm^{-3}), cobalt (13÷24.7 μg dm^{-3}), lead (61.2÷76.5 μg dm^{-3}), cadmium (7.81÷11.4 μg dm^{-3}), comparable contents of magnesium, calcium and copper as well as much lower contents of potassium (2.9÷7.2 mg dm^{-3}), phosphates (0.23÷0.5 mg dm^{-3}) and nitrates(V) (0.2÷0.26 mg dm^{-3}). In the period of the studies untreated municipal sewage was discharged to lakes of the Przemecki Landscape Park, which had a decisive effect on the results.

Studies were also conducted in the city of Poznan concerning heavy metal concentrations in waters of reservoirs located in the urban conurbation [19]. In the years 2006-2007 analyses were performed for the concentrations of 4 heavy metals (Zn, Cd, Pb and Cu) in waters of 4 reservoirs (Lakes Kierskie and Strzeszynskie, the Rusalka water body and the Solacki Pond). The highest contents were found for zinc (mean 159.61 μg dm^{-3}), lead (13.85 μg dm^{-3}), cadmium (0.048 μg dm^{-3}) and for copper (5.58 μg dm^{-3}). These contents were higher than those recorded in this study (Tables 5 and 6) in relation to zinc and lead, comparable in case of copper and much lower in case of cadmium. Higher contents of cadmium in waters of water bodies typical of agricultural areas could have been caused by the too intensive fertilisation of fields with fertilisers based on phosphorites, containing cadmium.

Relatively low contents of heavy metals were recorded in waters of the Retention Reservoir in Psurow in 2006. This reservoir is located in the Opolskie province near the village of Psurow in an agricultural area. Water samples were collected from 3 sites (at the inflow, at the height of the right inlet and at the dam). Recorded contents of heavy metals in waters amounted to: Zn 10÷11 μg dm^{-3}, Cu < 2 μg dm^{-3}, Cd < 1 μg dm^{-3}, Ni < 6 μg dm^{-3}, Pb < 3 μg dm^{-3} and Cr < 8 μg dm^{-3} [20]. They were the closest results to those recorded in waters of the small water bodies in the Gen. Dezydery Chlapowski Landscape Park. However, mean copper contents in waters of small water bodies located in the Landscape Park were two times higher than in the discussed retention reservoir.

When analysing different water ecosystems we need to take into consideration also those of very large areas. Studies conducted by Nguyen et al focused on the water of the largest lake in Hungary and at the same time in Central Europe [21]. In Lake Balaton analyses were conducted on water samples collected from different parts of that reservoir. It turned out that heavy metals do not pose a considerable threat for that lake. Contents of soluble forms of nickel, copper and zinc in waters in the years 2000-2002 did not exceed 1 μg dm^{-3}, that of lead 0.15 μg dm^{-3}, cobalt 0.07 μg dm^{-3} and cadmium 0.002 μg dm^{-3}. Water bodies of considerable area and capacity are much more resistant to inflowing pollutants in comparison with small water bodies.

Interesting studies were conducted by Guhathakurta and Kaviraj [22] in north-eastern part of the coast of India. They analysed heavy metal contents in waters, bottom deposits, prawn and fish in the ecosystem of brackish waters, formed by the flooding of nearby hollows by salt waters from the Bay of Bengal. Salt water mixed with fresh water supplied by rivers. Ponds are of considerable economic value, eg giant tiger prawn is cultured there. Those waters also had low contents of heavy metals, with the highest concentration recorded for iron at 14÷175 μg dm^{-3}, zinc 0.21÷9.67 μg dm^{-3}, lead 0.03÷0.2 μg dm^{-3} and cadmium 0.04÷0.11 μg dm^{-3}. They were markedly lower levels in comparison with waters in the analysed water bodies from the agricultural ecosystems.

Studies concerning heavy metals were also conducted in natural lakes of Malaysia. Climatic conditions have a considerable effect on those ecosystems. In that region annual precipitation ranges from 1.488 to 3.071 mm and to a considerably degree influences conditions found in those ecosystems. Lake Chini is located in the eastern part of the Malayan Peninsula. Analyses concerning heavy metal contents were performed by Ebrahimpour and Mushrifah in the period from October 2004 to July 2005 [23]. Mean contents of metals in lake waters ranged from 1.5 to 8.36 μg dm^{-3} for Cu, from 2.85 to 15.18 μg dm^{-3} for Pb and from 0.05 to 0.32 μg dm^{-3} for Cd. When comparing these concentrations with the contents in waters of the reservoirs in this study (Tables 5 and 6) it may be stated that water bodies in agricultural ecosystems contained much lower amounts of Pb and comparable amounts of Cu and Cd.

In Africa interesting studies were conducted in Nigeria. The objects of studies by Oyewale and Musa, comprised two main reservoirs in Nigeria located on the River Niger, ie the Kainji reservoir of 130 km in length and 24 km in width and Lake Jebba with a markedly smaller area [24]. The Kainji reservoir was constructed in December 1968 on the River Niger and it is of considerable importance for the generation of electricity. Both lakes are of economic importance for Nigeria. In that study analyses were focused on contents of elements posing a threat to surface waters and fish. The following contents of pollutants were recorded in the waters: Cu 0.7÷1.58 μg dm^{-3}, Co 1.09÷1.33 μg dm^{-3}, Cr 1.91÷2.43 μg dm^{-3}, Fe 11.4÷14.8 μg dm^{-3}, Mn 6.42÷14.8 μg dm^{-3}, Ni 0.79÷1.12 μg dm^{-3}, Pb 0.88÷1.67 μg dm^{-3}, Sb 2.72÷4.32 μg dm^{-3} and Zn 0.65÷1.1 μg dm^{-3}. They were lower or comparable levels to contents recorded in waters of water bodies from agricultural ecosystems (Tables 4, 5 and 6), with the only exception being cobalt, which concentration in waters of the reservoirs in Nigeria was more than 4 times higher.

Ions of elements being micropollutants in aquatic ecosystems are found at different concentrations in waters. The above comparison showed that the amounts of elements (mainly heavy metals) in waters depend mainly on the degree of anthropogenic pollution of these ecosystems. Other significant factors include also the type of the ecosystem (in large inland reservoirs concentrations of ions of elements in waters are generally lower), climatic conditions and the subsoil, on which the water body is located.

When comparing contents recorded in the thirteen small water bodies in the Gen. Dezydery Chlapowski Landscape Park with boundary values for water quality indicators from the group of substances particularly harmful for the aquatic environment (Tab. 9) it may be stated that contents of aluminium and lead in waters of forest water bodies nos. 1 and 2 were exceeded in the first and at the beginning of the second year of analyses. The other levels of analysed elements in those waters were below the boundary values.

Table 9

Boundary values of water quality indicators from the group of substances particularly harmful for the aquatic environment [15]

No. of water quality indicator	**Name of indicator**	**Unit**	**Boundary values of chemical water quality indicators according to categories of uniform surface water bodies**
4.3.1	arsenic (As)	[mg dm^{-3}]	0.05
4.3.2	barium (Ba)	[mg dm^{-3}]	0.5
4.3.5	chromium (Cr)	[mg dm^{-3}]	0.05
4.3.6	zinc (Zn)	[mg dm^{-3}]	1
4.3.7	copper (Cu)	[mg dm^{-3}]	0.05
4.3.10	aluminium (Al)	[mg dm^{-3}]	0.4
4.3.13	molybdenum (Mo)	[mg dm^{-3}]	0.04
4.3.14	selenium (Se)	[mg dm^{-3}]	0.02
4.3.15	silver (Ag)	[mg dm^{-3}]	0.005
4.3.16	thallium (Tl)	[mg dm^{-3}]	0.002
4.3.17	titanium (Ti)	[mg dm^{-3}]	0.05
4.3.18	vanadium (V)	[mg dm^{-3}]	0.05
4.3.19	antimony (Sb)	[mg dm^{-3}]	0.002
4.3.22	cobalt (Co)	[mg dm^{-3}]	0.05
Boundary values of chemical water quality indicators			
4.1.6	cadmium (Cd)	[μg dm^{-3}]	0.45÷1.5
4.1.20	lead (Pb)	[μg dm^{-3}]	7.2
4.1.23	nickel (Ni)	[μg dm^{-3}]	20

Conclusions

1. When analysing 22 elements dissolved in waters of the 13 water bodies the highest contents were shown for Na, K and Ca, while the lowest for Co, Cd, Ag, Se and Tl. Analysed elements may be ordered as follows: Na > K > Ca > Mg > Fe > Mn > Sr > Al > Ba > Zn > Li > Cu ≥ Ni ≥ As > V ≥ Cr ≥ Pb > Co ≥ Cd > Ag > Se ≥ Tl. The highest concentrations were found for the elements serving important functions in biotic components of aquatic ecosystems (Na, K, Ca and Mg), while the lowest contents in waters were observed for toxic elements towards living organisms (Cd, Ag and Tl).

2. Exceeded boundary water quality indicators from the group of substances particularly harmful for the aquatic environment specified in the Ordinance of the Minister of the Environment of 2008 were recorded for Al and Pb in waters of water bodies nos. 1 and 2.
3. The highest contents of nitrate(V) nitrogen were recorded in waters of water bodies nos. 4, 9 and 10, while those of phosphate phosphorus in waters of water bodies nos. 6, 7, 8, 11 and 13. High contents of these biogens may have influenced an increase in the level of trophic states in those water bodies.
4. Location is a factor determining contents of elements identified in waters. For waters in the water bodies located in built-up areas the characteristic symptom was the presence of K, Na and Li. In waters of the forest water bodies mainly Fe, Al, Pb, Co and Zn predominated. The presence of K, Na and Li was characteristic of waters in the water bodies located in built-up areas.
5. In five water bodies (1, 2, 7, 11 and 13) the date of analyses had a significant influence on variation of investigated parameters in waters.
6. The greatest similarities in terms of investigated parameters (taking into consideration dependent and explanatory variables) were observed in waters of water bodies nos. 1 and 2. Strong similarities in terms of all the analysed variables were observed in water bodies nos. 7, 8 and 11 as well as nos. 4, 9 and 10.

Acknowledgements

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WPŁYW CZYNNIKÓW ŚRODOWISKOWYCH NA POZIOMY MIKROZANIECZYSZCZEŃ W WODACH MAŁYCH ZBIORNIKÓW

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Abstrakt: Małe zbiorniki wodne pełnią bardzo ważną funkcję w krajobrazie. Niestety, wiele z nich jest silnie zanieczyszczonych bądź ulega likwidacji. Badania prowadzono na trzynastu małych zbiornikach wodnych położonych na terenie Parku Krajobrazowego im. gen. D. Chłapowskiego. Zbiorniki różniły się położeniem w krajobrazie, parametrami morfometrycznymi (głębokością, kształtem, powierzchnią) oraz roślinnością wodną i bagienną. Część z nich to typowe zbiorniki krajobrazów rolniczych, leśnych, pozostałe to zbiorniki położone na terenach wiejskich i w parkach. Celem przeprowadzonych badań była analiza poziomu zanieczyszczenia wody zbiorników pod względem zawartości pierwiastków oraz biogenów. Badania zmierzały do wyjaśnienia, jakie zmienne środowiskowe (zależne, objaśniające) wpływają na rozkład badanych parametrów w wodach małych zbiorników. Analizowano poziomy stężeń pierwiastków śladowych (Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Ag, Cd, Ba, Tl, Pb oraz Na, K, Fe, Ca, Mg), a także wartości pH w wodzie trzynastu zbiorników. Analizy prowadzono w latach 2008-2010. Cykl badawczy kończyły analizy azotu amonowego, azotynów, azotanów i fosforanów dla wody wszystkich zbiorników. Powyższe parametry zostały poddane analizie statystycznej, dla których wykonano modele RDA uwzględniające zmienne zależne oraz objaśniające.

Słowa kluczowe: zbiornik wodny, pierwiastki śladowe, biogenny, model RDA

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VARIA

CENTRAL EUROPEAN CONFERENCE ECOpole'11
Short Conference Report

The Conference ECOpole'11 was held in 13-15.X.2011 at the Conference Center „Rzemieslnik" in Zakopane, PL. It was the jubilee - the twentieth ecological conference of the series of meetings organised by the Society of Ecological Chemistry and Engineering, Opole, PL.

178 participants, including delegates representing 10 countries (Bulgaria, Czech Republic, Germany, Latvia, Lithuania, Poland, Romania, Russian Federation, Slovakia and Ukraine) took part in the event and presented 30 oral contributions and 177 posters.

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

The Conference issue of the quarterly *Ecological Chemistry and Engineering S* 2011, **18**(3) containing among others keynote speakers papers, was distributed at the Conference Reception desk together with a PenDrive (containing short info on Keynote Speakers, Abstracts of the Conference presentations as well as ECOpole'11 Conference Programme).

On Wednesday (12th October 2011) at 20.30 the participants were invited for Get-Together Party.

The Conference Agenda was divided into 5 sections:

* SI Ecological Chemistry and Engineering
* SII Environment Friendly Production and Use of Energy
* SIII Risk, Crisis and Security Management
* SIV Forum of Young Scientists and Environmental Education
* SV Health, Ecology and Agriculture.

The Conference was opened by prof. Maria Waclawek, Chairperson of the Organising Committee and prof. Witold Waclawek, Chairman of the Scientific Board and President of the Society of Ecological Chemistry and Engineering.

Prof. **Paul Jozef CRUTZEN** (*Max-Planck-Institute for Chemistry, Mainz, DE*), the **Nobel Prize Winner**, initiated the First Plenary Session with the invited lecture: "Atmospheric chemistry and climate in the Anthropocene". This contribution was met with great interest of the audience.

During the conference the plenary lectures were also delivered by other invited lecturers: prof. **Marina V. FRONTASYEVA** (*Joint Institute for Nuclear Research, Dubna, RU*): "NAA for Life Sciences at Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research in Dubna", prof. **Hartmut FRANK** (*University of Bayreuth, Bayreuth, DE*): "Fresh water pearl mussels, vanishing witnesses of water quality", prof. **Jozef LEHOTAY** (*Slovak Technical University, Bratislava and University of SS Cyril and Methodius in Trnava, SK*): "Trace analysis of some toxic compounds by HPLC" and prof. **Bogdan ZYGMUNT** (*Gdansk University of Technology, Gdańsk, PL*): "Increasingly green approaches to determine selected trace organics in complex matrices".

There were also presented very interesting lectures, *eg*: **S. Ledakowicz and L. Bilinska** (*Lodz University of Technology, Łódź, PL*): "Application of the Fenton reagent in the textile wastewater treatment under industrial conditions", **A. Nowak** (*West Pomeranian University of Technology, Szczecin, PL*): "Are the bacteria necessary in the environment?", **M. Bratychak** (*Lviv Polytechnic National University, Lviv, UA*):

"Utilization ways of by-products of hydrocarbon raw material pyrolysis", **S. Bocian and B. Buszewski** (*Nicolaus Copernicus University, Torun, PL*): "The new approach to the retention mechanism in reversed-phase liquid chromatography", **D. Panasiuk, A. Glodek and J.M. Pacyna** (*NILU Polska Ltd., Norwegian Institute for Air Research Branch Poland, Katowice, PL*): "Scenarios of mercury emission to air, water and soil in Poland to year 2020", **G. Boczkaj, M. Jaszczolt and M. Kaminski** (*Gdansk University of Technology, Gdansk, PL*): "New methods for process control of the thermal cracking rate of vacuum distillates and products from crude oil vacuum distillation", **E. Kraleva, V. Karamfilov and G. Hiebaum** (*Institute of Biodiversity and Ecosystem Research - BAS, Sofia, BG*): "Determination of polycyclic aromatic hydrocarbons in the Black Sea water by GC/MS following preconcentration with solid-phase extraction", **K. Piotrowska, M. Imbierowicz and A. Chacuk** (*Lodz University of Technology, Łódź, PL*): "Wet oxidation of dairy sewage: the kinetic study of intermediate products decomposition", **M. Siemieniec, H. Kierzkowska-Pawlak and A. Chacuk** (*Lodz University of Technology, Łódź, PL*): "Reaction kinetics of CO_2 in aqueous ethylethanolamine and methyldiethanolamine solutions using the stopped-flow technique", **R. Slavik, M. Julinova, and M. Labudikova** (*Tomas Bata University, Zlin, CR*): "Screening of the spatial distribution of risk metals in topsoil from an industrial complex" and **A.I. Stoica and A.A. Ciucu** (*University of Bucharest, Bucharest, RO*): "Kinetic approach for heavy metals detection by glucose-oxidase inhibition studies".

Thursday, a day of hard work, was finished with the Poster Session of the Section The Quality of Environment and its Monitoring. Many of the discussions started at the posters, lasted until the evening hours.

The next point of Thursday Conference Programme was the 45 minutes-long Musical Soirée. Songs and dances from Rocky Podhale were presented by highlander team „Młode Klimki". The audience applauded the players and claimed for encore.

At 20.00 the Conference participants were invited for a Conference Dinner.

As usually during the ECOpole Conferences, the second day included the Session of the Young Scientists (a forum of young scientists that present and discuss local ecological problems of their countries). During the Young Scientists', Environmental Education and Renewable Energy Poster Session 57 posters were presented.

The Scientific Board (**prof. Stanisław Ledakowicz** (*Lodz University of Technology, Łódź, PL*), **prof. Mikhail Bratychak** (*Lviv Polytechnic National University, Lviv, UA*), **prof. Bohumil Vybiral** (*University of Hradec Kralove, Hradec Králové, CZ*) and **prof. Witold Waclawek** (*Society of Ecological Chemistry and Engineering, Opole, PL*)) granted awards (sponsored by the Society of Ecological Chemistry and Engineering) for the best presentations. The award for oral presentation was given to **Anna Kwiecinska,** MSc (*Silesian University of Technology, Gliwice, PL*) for the oral A. Kwiecinska and K. Konieczny: "Application of membrane processes in treatment of slurry from high-density pig farming". The awards for poster presentations were given to **Lucie Trnkova**, MSc (*University of Hradec Kralove, Hradec Kralove, CZ)* for the poster: L. Trnkova, I. Bousova, F. Altieri and J. Drsata: "Interaction of proteins with low-molecular substances occurring in environment: Structure-activity relationships", to **Agnieszka Baran**, MSc (*University of Agriculture, Krakow, PL*) for the poster: A. Baran and M. Tarnawski: "Content of heavy metals in leachate from bottom sediments as a potential source of contamination of water and ground environment" and to **Aleksander Zaremba**, MSc (*Czestochowa University of Technology, Czestochowa, PL*) for the poster: T. Rodziewicz, J. Nakata, K. Taira, I. Inagawa, A. Zaremba and M. Waclawek: “Performance of flat module made of Sphelar cells in higher latitude areas”.

On Saturday morning an excursion was organised to Kuznice. Participants visited Manor-Palace in Kuznice, Memorial Chamber of Count Wladyslaw Zamoyski and an exhibition of works by Antoni Kocjan “Animals of the Tatras”.

Closing the conference, prof., prof. Maria and Witold Waclawek made short recapitulation. In general, ECOpole’11 was focused on monitoring of the quality of natural environment, its effects on human life, environmental education as well as application of renewable sources of energy.

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

They asked the participants to publish electronic version of presented during ECOpole’11 Conference contributions (oral presentations as well as posters) at the conference website ecopole.uni.opole.pl - some persons have already took advantage of this call.

They announced, that full texts of the presented papers will be published (after obtaining reviewers’ positive opinions) in the successive issues of the journals *Ecological Chemistry and Engineering A* and *S* and they will be distributed to all participants. The Extended Abstracts of the presentations will be published in two subsequent issues of semi-annual *Proceedings of the ECOpole*.

Thanks to the financial support of the Polish Ministry of Scientific Research and Higher Education, it was possible, among others to publish Abstracts and full Conference contributions on the Conference website.

At the end they invited all Colleagues to attend the ECOpole’12 Conference, which will be held at the Conference Center „Rzemieslnik” in Zakopane, PL in the next October.

Maria Wacławek

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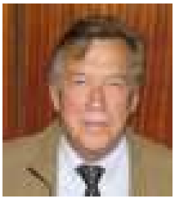
Invited Lectures

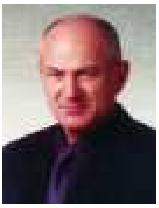
Jozef Crutzen - Atmospheric chemistry and climate in the Anthropocene

Marina V. Frontasyeva - NAA for Life Sciences at Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research in Dubna



Hartmut Frank - Fresh water pearl mussels, vanishing witnesses of water quality

Jozef Lehotay - Trace analysis of some toxic compounds by HPLC



Bogdan Zygmunt - Increasingly green approaches to determine selected trace organics in complex matrices

Professor Paul Jozef Crutzen, the Nobel Prize Winner, delivering his lecture

Professor Marina V. Frontasyeva as a Chairperson

INVITATION FOR ECOpole'12 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 21st annual Central European Conference ECOpole'12, which will be held in 11-13 X 2012 (Thursday-Saturday).

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

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

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format)
- extended Abstracts (4-6 pages) in the semi-annual journal *Proceedings of ECOpole*
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

Additional information one could find on Conference website

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15th July 2012** and for the Extended Abstracts: **1st October 2012**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2012**) on the Conference website.

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

At the Reception Desk each participant will obtain abstracts of the Conference contributions as well as the Conference Programme recorded on electronic media (the Programme will be also published on the ECOpole'12 website).

Further information is available from:
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20. 2011 CEC ECOpole'11 Zakopane

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In preparation of the manuscript please follow the general outline of papers published in the most recent issues of *Ecol. Chem. Eng. S*, a printed sample copy can be sent, if requested. Papers submitted are supposed to be written in English language and should include the title, an abstract and keywords, if possible also in Polish language. If not then the Polish title, abstract and keywords will be provided by the Editorial Office. The manuscript should contain also text, figures, tables and reference list.

Generally, a standard scientific paper is divided into:

- Introduction: you present the subject of your paper clearly, indicate the scope of the subject, present state of knowledge on the paper subject and the goals of your paper;
- Main text (usually divided into: Experimental - you describe methods used; Results and Discussion);
- Conclusions: you summarize your paper;
- References.

The first page should include the author's (authors') given name(s) without titles or scientific degrees like Prof., Ph.D., etc., their affiliations, phone and fax numbers and their email addresses however, with the corresponding author marked by an asterisk.

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[l] Trapido M, Kulik N, Veressinina Y, Munter R. Water Sci Technol. 2009;60:1795-1801. DOI: 10.2166/wst.2009.585.

[2] Lowe DF, Oubre CL, Ward CH. Surfactants and cosolvents for NAPL remediation. A technology practices manual. Boca Raton: Lewis Publishers; 1999.

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