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SPIS TREŚCI

VARIA

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Paweł ŚWISŁOWSKI[1], Małgorzata RAJFUR[1*]
and Tadeusz RODZIEWICZ[1]

ASSESSMENT OF EFFECTIVENESS OF THE PHOTOVOLTAIC SYSTEM INSTALLED ON THE ROOF OF THE UNIVERSITY OF OPOLE BUILDING

OCENA EFEKTYWNOŚCI SYSTEMU FOTOWOLTAICZNEGO ZAINSTALOWANEGO NA DACHU BUDYNKU UNIWERSYTETU OPOLSKIEGO

Abstract: The objective of the carried out study was to analyse and assess effectiveness of the photovoltaic system installed on the roof of the University of Opole building at ul. Kominka 6 in Opole. The scope of the study included an assessment of: power generation – the relation between the panels location and energy yield (quantity of generated electric power and geographical location of photovoltaic panels), economic – the period of return on investment and ecological – *ie* how much larger the emission of carbon dioxide by the power plant would be during electric power generation, without work of the photovoltaic system. The studies showed good energy yield of the PV installation, typical return on investment period and ecological aspect of the project, *ie* a considerable reduction of CO_2 emission to atmosphere.

Keywords: renewable energy sources, RES, photovoltaics, photovoltaic panels, effectiveness of PV system, PV cell

Introduction

In consequence of many years of mining and using fossil fuels, a new threat to natural environment appeared. Irrational use of non-renewable sources of energy, such as coal, oil or gas influenced deterioration of natural environment quality by, for example, constant presence of many harmful substances, dust and volatile compounds in atmospheric aerosol, which negatively influence the planet's ozone layer, resulting in irreversible degradation of natural environment. More and more frequent occurrence of

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violent storms alternatively with severe droughts is evidence of weather anomalies, which have recently increased their intensity. They are probably caused by the greenhouse effect, which is caused mainly by the emission of toxic products of combustion (CO, CO_2, NO_x) and other greenhouse gases. A number of fauna and flora species may die out, in consequence of the gradual degradation of natural environment. The observed climate changes are not distant and strange phenomena; also in our country changes can be noticed, in particular in seasons: winters, which have been getting warmer in recent years and hot summers, with extreme high air temperatures. Considerable increase of temperatures in Poland may result in increasing of the Baltic Sea water levels, posing a threat to many coastal seas. Therefore, the dangers caused by anthropogenic activities, may influence not only the world of fauna and flora but also human lives. In view of these dangers, many countries have undertaken steps in order to limit the influence of human civilisation on the climate of our planet. Signing the December protocol in Kyoto in 1997 is one of such activities. On the basis of this agreement related to counteracting global warming, the role of renewable energy sources (RES) increased considerably. Searching for alternatives to fossil fuels became the priority in order to reduce quantities of pollution emitted to the atmosphere. For this purpose, regulations concerning allowed emission limits of pollution from combustion have been introduced and fines for environment pollution have been increased. However, these are the solutions which are applied on the industrial scale and in relation to a whole state policy; there are also methods of individual counteracting the climate changes such as, for example reducing consumption of technical goods or using energy-saving appliances. One of such prospective technologies is the use of solar power converted into electric energy in photovoltaic cells. These technologies have become more and more popular not only because they make it possible to generate electric energy without any side-effects such as pollution, noise or other factors, which would negatively influence natural environment [1–3].

Transformation of solar power into electric energy is possible in photovoltaic cells. This is possible thanks to the photovoltaic phenomenon discovered in 1839 by the French physicist Alexander-Edmond Bequerel [4], also known as "Bequerel's phenomenon." The photovoltaic phenomenon (photovoltaic effect, conversion) is based on generation of electrical charge carriers by the material, which absorbed solar beams. A typical photocell made by thick film PV technology is a rectangle semiconductor silicon plate (crystalline, polycrystalline), with the potential barrier formed by, for example, a built-in p-n junction. More information regarding construction of typical PV cells designed for common use can be found in [5–8].

A single PV cell can supply power only to receivers with low current consumption. The power of a standard PV cell, depending on the type and in normal conditions, is within the range of approximately 1–1.5 W at the voltage of 0.5–0.6 V and intensity of about 2 A. A PV cell, as the source of direct electric current, can be easily connected in parallel or series connections, into the systems with higher powers, commonly known as solar panels. Cells are connected in parallel, in order to increase the current. By connecting PV cells in series, a higher voltage is obtained at the exit of the set up. By connecting PV cells in larger systems – modules, solar panels, series, etc., it is possible

to adjust parameters of the generated electric energy to the requirements of the receivers or electric grid. Standard modules available in the market most often contain from 36 to 44 PV cells connected in series. Their typical power is within the range from 12 to 300 W. The professional PV generators use modules with capacity from 250 to 300 Wp. More information on the PV modules construction and PV matrices can be found in [7, 9].

Photovoltaics has been developing very dynamically all over the world and, after water and wind power industries, it is the third technology, as far as the installed power is concerned, which uses RES. The top ten manufacturers of PV cells and modules in the world are: Q-Cells (Germany), Sharp (Japan), Suntech (China), Kyocera (Japan), First Solar (USA), Motech (Taiwan), Sanyo (Japan), SunPower (USA), Yingli Solar (China), Solarworld (Germany/USA) [10, 11].

The condition of photovoltaics in different European Union countries vary considerably, mainly due to different policies and support programs in the sector of renewable energy sources. Germany has been the leader in the European market (EU27) for over 10 years – with more than 80%, installed capacity of 1100 MW and annual energy output of 3.07 TWh [59]. There are two large PV power plants operating in Germany: Strasskirchen (54 MW) and Lieberose (53 MW). The PV power plant near Leipzig built in 2010, with the capacity of 40 MW cost 180 million EUR; it generates 970 kWh of energy every year from 1 kW of the installed power. By the end of 2012, capacity of the PV cells installed in Germany was approximately 32 698.0 MW (in the whole European Union – 68 647.2 MW); 28 TWh energy was generated, which was approximately 2.8% of the total electric energy demand [12, 13].

The production and assembly of PV modules during the years 2011–2012 in the European Union increased from 52 127.3 MW to 68 647.2 MW, from which only 3.4 MW in Poland. Within implementation of the decisions of the climate-energy package of 2008, the EU decided to increase the share of renewable energy in the total energy consumption by 20% (15% for Poland) until 2020, by providing financial aid to member states. Both private and public institutions are allowed to use the financial aid programs for installation of RES and University of Opole is one such example. University of Opole used the resources from the European Regional Development Fund within the Regional Operational Programme for the Opole Province during the years 2007–2013 and implemented Measure 4.3. Air protection, renewable energy sources, titled *Thermal modernization and installation of renewable energy source equipment – the University of Opole didactic building at ul. Kominka 6 in Opole.* The studies on commercial PV cells, focusing on the analysis of influence of various environmental factors on actual efficiency of the cells have been under way for several years at University of Opole, however, the above mentioned investment is of a practical nature and is used to generate renewable source electric energy for the needs of the building [12–14].

Considering that the installation works of the presented PV system were completed and it was commissioned for University of Opole, it became necessary to initiate studies of its efficiency and present the results and remarks regarding its operation.

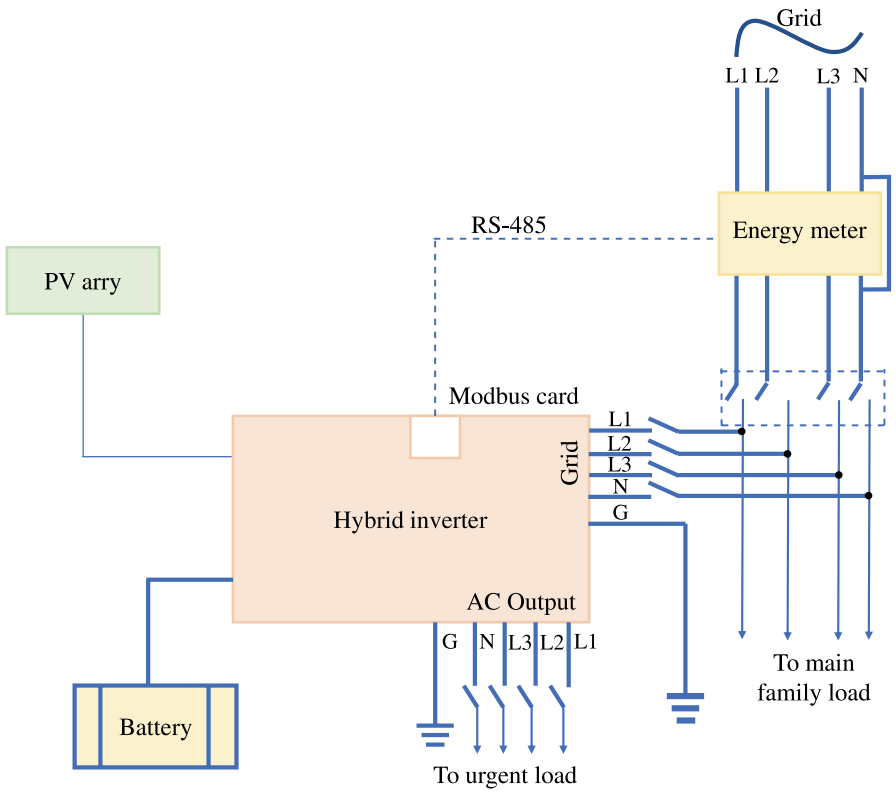

Fig. 1. The photovoltaic system diagram [15]

Fig. 2. A photograph of the PV system installed on the roof of University of Opole building (photo P. Świsłowski)

Materials and methods

The main objective of using the PV system was the reduction of electric energy use by the building users. During the design stage of the PV installation, its location and inclination were optimised, due to the occurrence of the potential shading of the installed PV modules by other buildings. This is an important issue because shading reduces insolation and, in consequence, the installation efficiency. In effect, the PV system was installed on the flat roof of the University of Opole didactic building at ul. B. Kominka 6, at the southern side. This is one of the two buildings owned by Independent Chair of Biotechnology and Molecular Biology (SKBiBM).

Location: Opole – 53,60^{o} N 19,32^{o} E
Level: 115.08 m above the sea level.
Modules inclination for the mounting system: 40^{o}, azimuth 0^{o}.

The PV system with total power of 4.50 kWp contains of 18 hybrid PVT type collectors (*Photovoltaic Thermal*) with 250 Wp power each.The PVT collector is a combination of a solar flat collector and a PV module, containing polycrystalline PV cells. The thermal solar collector converts solar radiation into heat energy, used for hoy water production and central heating, whereas the PV module converts solar into electric energy. The used frequency converter with 10 KWp contains two MPP tracker inputs. 2 strings, 4 modules each were connected to the input of the first MPP1 tracker and 2 strings, 5 modules each to the other MPP2 tracker. The estimated exploitation period of the FV system is 25 years. The PV system is maintenance-free and does not require any social facilities and water-sewage installations. Electric energy generated in PV cells will be used for the building's needs – lighting of communication routes with LED light sources (some items are equipped with 360^{o} movement sensors) and power supply to ventilation systems. The PV system will not emit noise or any pollution to environment. Considering the type of investment, there are no local or cross-border influences [15]. As the installed PVT collectors are hybrid (a combination of a solar and photovoltaic panel), this study shall focus only on the electric part, *ie* electric energy generation by the PV system. Fig. 1 presents the diagram of the discussed photovoltaic system. Fig. 2 presents the discussed photovoltaic system.

Fig. 3. A photograph of the frequency converter (photo P. Świsłowski)

The high-voltage, photovoltaic, hybrid, three-phase frequency converter InfiniSolar 10 kW with the function of energy storage can supply electric energy to users as well as power own technical equipment (*ie* the

solar system devices), with the use of: When the PV modules output power is sufficient, it is possible to simultaneously supply power to the user and to charge PV system own batteries and other technical devices [15] (Fig. 3).

Thermal upgrade and mounting the RES equipment for the University of Opole building at ul. Kominka 6 in Opole were completed in May 2015. The data was collected from September 2015 for one year, *ie* until September 2016. The data of the power generated by the PV system was collected on the last day of each month (except for Saturdays and Sundays, when access was impossible). The study activities involved retrieving the registered data with the use of SolarPower 1.07 computer software, which is dedicated to and compatible with the frequency converter of the system. With the use of the program it was possible to read the registered and generated electric energy data from the PV system.

Additionally, on the basis of literature, the energetic [16, 17], economic [18, 19] and ecological [20] analyses were carried out.

The energetic analysis was based not only on the data obtained from the PV system. In order to assess the energetic efficiency of the system, the quantity of the electric energy generated by PV cells was compared with the total quantity of electric energy used by the building. The data regarding energy consumption by the building were obtained thanks to cooperation with the Technical Department of University of Opole.

Thanks to the data obtained from Technical Department regarding costs of use of electric energy in the whole building, it was possible to calculate the economics of the renewable energy source installation program. The time of return on investment, considering the previously assumed PV system exploitation period, was calculated on that basis.

Thanks to the previously prepared results of the energetic analysis of the PV system, it is possible to draw the investment ecological benefits analysis. The objective of that analysis is calculation and assessment of CO_2 reduction, in consequence of electric energy generation by the PV system, instead of a conventional power plant, based on the previously obtained and analysed data.

Results and analysis

Table 1 presents the results of energy yield from the PV system installed on the roof of the University of Opole building.

The electric yield is the quantity of electric energy generated by the PV system during a defined period [21]. Table 2 presents a summary of daily energetic yield plus the sum of kWh electric energy generated during the whole month.

The data for the analysis regarding electric energy consumption in the building of Independent Chair of Biotechnology and Molecular Biology were obtained from University of Opole Technical Department. The data was collected and presented in Fig. 4.

Electric energy is used mainly for lighting didactic lecture rooms, sanitary, social and administration premises. Electric energy is also used to supply power to light sources in laboratories and other equipment, TV and radio equipment, domestic appliances and

Table 1

Energy yield from the photovoltaic installation in [kWh]

Year	2015				2016							
Month / Day	IX	X	XI	XII	I	II	III	IV	V	VI	VII	VII
	[kWh]											
1	26.2	31.5	24.7	2.39	0.23	1.00	0.68	4.02	31.2	36.7	31.7	20.6
2	14.0	29.6	23.6	0.12	8.21	2.82	17.7	37.3	30.7	20.3	31.7	32.1
3	29.5	27.2	23.3	1.82	9.18	6.56	0.86	31.7	15.9	15.4	19.5	18.7
4	14.4	26.4	21.3	10.5	0.49	4.12	3.61	31.6	3.60	30.1	31.4	34.6
5	24.2	20.2	11.8	13.2	0.75	6.25	14.1	30.7	30.1	28.8	25.6	17.6
6	8.78	18.4	8.96	14.5	2.95	16.8	5.05	15.0	36.7	35.0	23.5	9.92
7	20.4	8.52	1.33	0.44	0.36	21.5	1.44	17.8	35.9	37.5	30.1	29.6
8	23.3	13.1	20.9	0.56	5.78	8.82	3.14	2.20	26.0	36.9	25.5	35.9
9	23.4	10.9	1.43	1.59	8.05	17.3	3.60	0.79	24.9	19.1	20.4	19.4
10	18.3	25.5	0.72	8.99	9.68	0.60	5.41	0.61	38.4	21.3	31.7	6.47
11	14.7	12.8	1.02	8.00	1.31	4.17	0.30	9.78	31.4	18.0	27.0	28.5
12	31.2	2.45	2.14	12.5	0.43	7.86	0.34	5.92	27.8	32.1	16.6	23.5
13	29.5	1.39	14.6	1.42	3.66	1.21	2.58	24.5	20.2	13.0	22.4	11.1
14	21.8	1.10	19.4	8.05	2.69	19.5	27.0	2.23	24.7	19.8	2.93	22.9
15	19.3	1.41	0.88	0.59	9.39	1.13	2.49	19.1	24.8	24.5	10.2	24.4
16	21.2	15.0	0.50	3.25	1.05	0.98	32.6	8.55	25.1	31.4	10.9	15.8
17	31.7	1.08	1.19	0.57	5.00	0.70	32.8	23.7	12.9	25.1	20.1	29.6

Table 1 contd.

Year	2015				2016							
Month / Day	IX	X	XI	XII	I	II	III	IV	V	VI	VII	VII
	[kWh]											
18	8.55	14.9	1.27	2.45	6.46	0.51	32.0	20.3	17.0	36.1	4.76	25.1
19	29.7	5.51	1.79	10.8	14.6	0.42	23.4	11.0	23.8	28.9	13.5	22.9
20	9.48	1.07	1.88	12.9	0.42	16.0	2.33	29.4	22.9	3.41	26.0	27.6
21	25.0	1.92	1.27	3.26	1.02	2.87	12.8	38.9	35.1	22.6	35.7	3.77
22	29.3	3.72	5.45	4.54	19.9	12.8	5.79	38.9	35.4	35.0	35.0	18.3
23	10.7	6.24	6.36	12.5	7.30	1.49	22.2	25.5	36.9	31.0	30.3	25.4
24	17.8	24.7	17.6	11.2	0.76	17.5	21.9	21.3	28.7	34.6	16.1	27.2
25	19.8	3.45	10.5	3.57	0.36	1.27	14.0	28.8	24.5	31.6	15.4	36.1
26	8.48	9.14	0.44	9.30	1.52	7.48	8.18	25.9	8.49	12.0	18.3	36.1
27	19.4	22.4	4.46	4.03	3.97	20.1	37.2	7.09	28.7	10.8	18.0	34.5
28	25.7	24.3	13.0	3.84	0.34	5.89	25.7	26.8	22.5	28.3	18.8	34.7
29	24.4	2.96	1.93	1.33	17.0	0.26	23.7	10.9	8.69	27.3	10.9	24.8
30	5.97	0.002	2.23	6.24	3.23	—	10.8	n/a	28.2	11.4	n/a	30.2
31	—	n/a	—	n/a	n/a	—	2.02	—	11.5	—	n/a	4.07
Total	606	367	246	174	146	208	396	550	773	758	624	731

n/a – no data available.

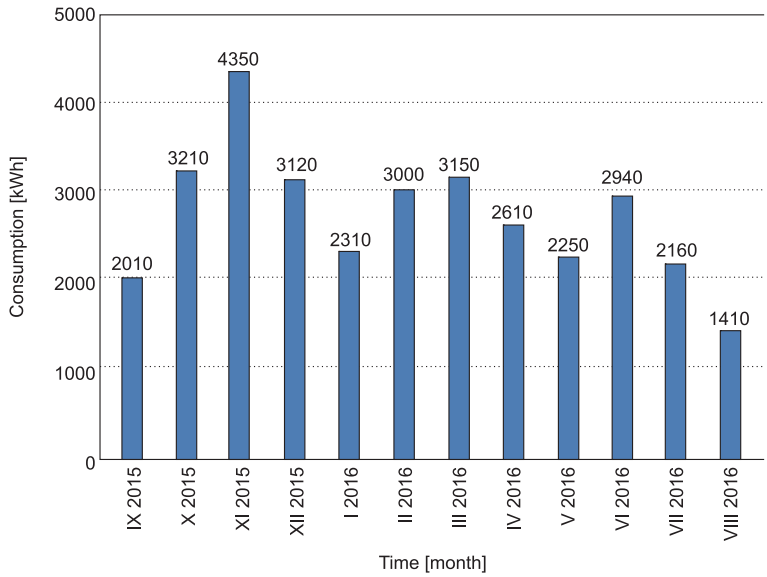

Fig. 4. Mean electric energy consumption in a year

ventilation systems. Electric energy is also used to power machines (grinders, among others) in workshops.

Table 2 presents the percent of covered energy demand with the use of the PV system.

Table 2

Electric energy demand coverage level

Year	Month	Yield [kWh]	Consumption [kWh]	Cover [%]
2015	September	606	2010	30.1
	October	367	3210	11.4
	November	246	4350	5.65
	December	174	3120	5.59
2016	January	146	2310	6.32
	February	208	3000	6.93
	March	396	3150	12.6
	April	550	2610	21.1
	May	773	2250	34.3
	June	758	2940	25.8
	July	624	2160	28.9
	August	731	1410	51.9
	Total	5579	32520	—
	Mean	465	2710	17.2

Table 2 presents percent coverage of electric energy demand by the photovoltaic system. As can be noticed, the new PV system cannot cover total demand for electric energy (it was designed to cover this demand in part).

The following assumptions were made for the calculation of profitability and exploitation of the PV system:

– electric yield of the installation during the first and subsequent years of operation 5.58 [MWh],
– electric energy price (stable) 0.54 [PLN/kWh],
– constant demand for electric energy for 25 years,
– PV installation cost 66 500 [PLN].

The diagram in Fig. 5 presents the time, after which return on investment is obtained.

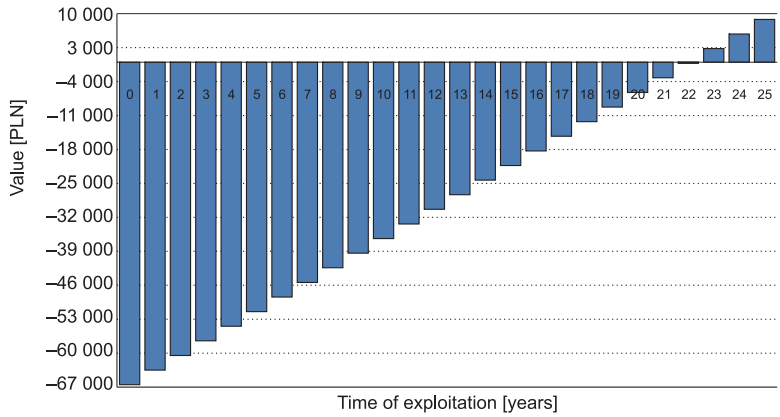

Fig. 5. Diagram of return on investment

Considering the assumptions, return on investment time will be 23 years, as presented in Fig. 5. During the 25 years of exploitation, the photovoltaic installation will generate 16.7 MWh of electric energy (after return on investment period) and the savings should amount to nearly PLN 9 000.

The ecological aspect of the renewable energy source installation is as follows: The emission index for the generated electric energy in combustion sources (from all fuels) is 823,257 kg · CO_2/MWh [20]. On the basis of the data from the National Centre for Emissions Management (KOBiZE) and own calculations, the annual reduction due to electric energy generation from the PV system (5.58 MWh) and not from a conventional power plant is 4.59 Mg of carbon dioxide. In turn, the 25 years of the photovoltaic installation operation shall bring emission to atmosphere reduction of nearly 115 Mg of CO_2.

Summary and conclusions

Renewable energy sources are a real alternative to fossil fuels for the production of electric and heat energy. The degree of their use in Poland has increased [22] despite the

fact that the regulations and energy policy do not give priority to RES. It would be a big challenge to start generating all or part of energy from renewable sources, however, they should be considered in the balanced energy mix. RES development is necessary not just to meet the EU requirements but also considering environmental issues. Ongoing degradation of nature and the increasing pollution with greenhouse gases emitted to the atmosphere cause that RES should be considered as an important element in the struggle against global warming.

The assessment of efficiency of the PV system installed on the roof of a didactic building of University of Opole at ul. Kominka 6 in Opole aimed at analysis of the energetic, economic and ecological effectiveness of the project.

As a result of the carried out study, the following conclusions have been reached:

1. The installed PV system partly covers the demand for electric energy, in line with the Investor's assumptions – University of Opole.

2. Location of hybrid collectors on the southern side, in Opole climate conditions, brought benefits in the form of energy yield of 5.58 MWh/years.

3. The return on investment for purchase and installation of RES is 23 years. From the Investor's point of view, it is a long-term investment; however, during 25 years of exploitation, the PV system generates financial gains.

4. Installing hybrid collectors causes emission reduction of 4.59 tons CO_2/year and 115 tons CO_2 in 25 years. The use of the photovoltaic system improves the image of the institution taking care of natural environment, by using the RES technology in counteracting climate changes.

5. Verification of the obtained data in further analyses of the collected results of energy yield shall allow to determine in more detail the efficiency of the installed PV system.

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OCENA EFEKTYWNOŚCI SYSTEMU FOTOWOLTAICZNEGO ZAINSTALOWANEGO NA DACHU BUDYNKU UNIWERSYTETU OPOLKIEGO

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Abstrakt: Celem przeprowadzonych badań była analiza i ocena pracy wydajności systemu fotowoltaicznego zainstalowanego na dachu budynku Uniwersytetu Opolskiego przy ul. Kominka 6 w Opolu. Zakres pracy obejmował ocenę: energetyczną – zależność usytuowania paneli a uzysk energetyczny (ilość wyprodukowanej energii elektrycznej a położenie geograficzne paneli fotowoltaicznych), ekonomiczną – czas zwrotu poniesionych nakładów inwestycyjnych oraz ekologiczną: tj. ile elektrownia wyemitowałaby więcej dwutlenku węgla do atmosfery w wyniku produkcji energii elektrycznej bez udziału tego systemu fotowoltaicznego. Badania wykazały dobry uzysk energetyczny instalacji PV, typowy okres zwrotu poniesionych nakładów na inwestycję oraz na ekologię przedsięwzięcia w postaci znacznej redukcji emisji CO_2 do atmosfery.

Słowa kluczowe: odnawialne źródła energii, OZE, fotowoltaika, panele fotowoltaiczne, efektywność systemu PV, ogniwo PV

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AMBIENT AIR QUALITY FOR DIFFERENT WEATHER CONDITIONS IN TWO SITES OF OBSERVATION

JAKOŚĆ POWIETRZA DLA ODMIENNYCH WARUNKÓW POGODOWYCH W DWÓCH MIEJSCACH OBSERWACJI

Abstract: This paper presents the results of a short-term study into the variability of air quality corresponding to a variety of weather conditions in two observation spots differing in terms of urban development and land use character. The project reported here was conducted in the areas of housing development in the rural and urban areas during the cold season. The analysis involved 384 independent, 60-minute registrations of core air pollutants (NO_2, SO_2, O_3 and PM10). The research applied reference methodologies applied for measurements of physical parameters. The results of the registrations were compared by application of the Common Air Quality Index (CAQI) and the results were verified and analyzed by non-parametric tests (Spearman correlation and Wilcoxon ranked pair test). Consequently, it was stated that the comparison of air quality parameters by the application of the CAQI index provides an adequate solution. It was also observed that the short-term variability of the air quality parameters in the measurement spots is strictly related with the weather conditions in a given location. It was also concluded that during the cold season, the degree of urban development of the residential areas does not have a decisive effect on the course of the profiles of the core pollutants registered during one day. As a result, it was indicated that PM10 forms the source of pollution and determines the overall air quality. The study also revealed that air quality in the inhabited rural areas does not differ much from the more populated residential area in the town.

Keywords: winter, city, village, air quality, core pollutants, NO_2, SO_2, O_3, PM10

Introduction

The works containing reports into short- and long-term air quality in the vicinity of human dwellings provide a wide range of information regarding the sources of pollution, transformation of pollutants and their impact on human health [1–3]. A common direction of such study involves the determination of the impact of urban development on the local variations of the climate and aerosanitary conditions [4]. The

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processes occurring during chemical transformations and harmful impact of the primary pollutions are some of the topics that have been treated in depth and hence are well researched [5]. For a few decades, the parameters of air quality are expressed in relation to the admissible levels of the mass concentrations of core pollutants, including nitrogen dioxide, sulphur dioxide, ozone and particulate matter. In the urban domestic area, the principal sources of these pollutants include fossil fuel combustion from both stationary sources, *ie* power generation and mobile sources, *ie* transport. Tropospheric ozone (O_3) is a secondary pollution produced mainly by complex photochemical reactions occurring in the polluted air, for example with nitrogen oxides (NO_x) [6].

Apart from the determinants resulting from the manner in which useful energy is generated, the level of imission is affected by the weather conditions and characteristics of a given climate [7–9]. In the Central and Eastern Europe (in the moderate and subpolar climate) the greatest levels of pollutants are observed during the cold season, in particular on artic and windless days [10]. Another aspect is associated with the fact that the air quality and structure of emission sources (*eg* in Poland) is distinct from the ones that are recorded in the towns in Western Europe [11]. This pertains to both urban and rural areas. For instance in European rural areas most of PM comes from long-distant pollutant transport and natural sources. Its concentration is generally lower than in city centers and rarely causes any air quality problems [12–14]. In Poland, these conditions are completely distinct, which leads to a great deal of research focusing on the air quality in the winter months [10, 15, 16].

One of the ways to present the result is to apply air quality indices. Such indices are usually applied with the purpose of comparing aerosanitary conditions in towns. However, they can be successfully applied to verify the air quality in the rural areas, as well as in remote locations [17]. At present, studies offer an extensive use of the CAQI index [18], which describes the short- and long-term differences in the aerosanitary conditions in the locations selected for comparative purposes.

The objective of this work is to report on the results of study involving a comparison of the air variability for a variety of weather conditions in two observation sites with distinct characteristics in terms of urban development and land use character. This comparison applied Common Air Quality Index (CAQI) and statistical analysis. The result of the study took the form of the statements whose aim was to verify the following research hypotheses: – *during winter, for various aerosanitary conditions, the hourly variations in the air quality in a given location do not demonstrate statistically significant differences over the 24-hour period* (1), – *during winter, for identical weather conditions the degree of urban development do not affect the profile of the variability of the one-hour values of the parameters characterizing ambient air quality* (2).

Materials and methods

Measured pollutants, measurement sites and monitoring period

The study into the variability of the basic air quality parameters was undertaken in two sites. The observation spots were distinct in terms of the degree of urban

development and domestic heating systems use character. The measurements values of the concentrations of core air pollutants (SO_2, NO_2, O_3 and PM10) performed concurrently over 1-hour periods were accompanied by registrations of the remaining meteorological parameters (atmospheric pressure P, wind speed and direction W, temperature T, rainfall R, relative humidity RH), which were collected for both urban and rural areas. The registration in the rural area were realized in the centre of village Kotorz Maly (Poland, 50°43′50″ N; 18°02′36″ E; 1025 inhabitants). The measurement point was located in direct neighborhood of compact rural building development area and main country road. All households in the rural area comprise individual energy and hot water supply systems. The representative data regarding the concentrations of the gaseous pollutants for the urban area (provincial town of Opole, Poland, 50°40′36″ N; 17°57′01″ E, 122,000 inhabitants), were gained from the air monitoring system managed by the Voivodeship Inspectorate of Environmental Protection (WIOS) [19]. The monitoring station of WIOS is situated in the centre of the biggest housing estate area in Opole city. As it has a population of around 20,000 people (8510 households spread around 134 buildings), the areas under this study are surrounded by a ring road with a high traffic volume. In contrast, all flats in the area under measurement apply heat derived from a district heating system.

The measurements and registrations were performed over 2 weeks throughout the period from January 9th to 22nd, 2017. The relative location of the two measurement spots in the vicinity of one another does not imply statistically significant differences in terms of the parameters defining weather conditions in the urban and rural areas. The verification of the research hypotheses applied a range of days which varying in terms of the weather conditions, *ie* January 11th, 2017 (a) and January 20th, 2017 (b). The weather in the denoted as "a" were characterized by unstable weather; T = 1–11°C, changeable western wind (W = 3–11 m/s), low value of pressure (P = 984–992 hPa) and variable humidity (RH =72–87%). For the case of the conditions defined as "b", greater weather stability was observed, however, considerable differences were present in comparison to the weather parameters defined for the date "a" [T = (–8)–(13)°C; W = 0–1 m/s (N); P = 1028–1031 hPa; RH = 68–71%). In both cases, no instances of precipitation were recorded in the periods applied in this study.

The methodology of sampling and data analysis

The study applied data from automatic measurement equipment realizing reference methodologies with the purpose of measurement of the mass concentrations of the physical parameters. In all cases, registrations were performed on an hourly basis over the entire period of the day. During the observations conducted in the rural areas, the mass concentrations of O_3, SO_2 and NO_2 were measured and registered by application Aeroqual AQM 60 apparatus [20]. The data regarding the mass concentrations of the gaseous pollutants in the urban area applied an automatic measurement station managed by the Voivodeship Inspectorate of Environmental Protection [19]. The mean hourly concentrations of PM10 in both locations were determined on the basis of the measurements by means of DustTrak DRX 8533 optical dust meters [21]. The

information regarding the remaining aerosanitary parameters was gathered by the use of a portable Davis® weather station.

The data that was gathered was subsequently processed for further analysis. The Shapiro-Wilk test of normality demonstrates that the values of the particular parameters in the registration sites are not characterized by normal distribution. The further analysis of the data from the measurements applied non-parametric tests. The data that was adapted for the purposes of the statistical analysis was rescaled in accordance with the algorithm (1), as a results of which the impact of the absolute value of a given variable was reduced and the value of the variables were maintained in the range {0;1}.

$$x' = \frac{x - x_{\min}}{x_{\max} - x_{\min}} \tag{1}$$

The correlations between the variables were measured by the Spearman test, whereas the research hypotheses were verified by the Wilcoxon signed-rank test. For all cases significance level of 0.05 was adopted.

Results and discussion

Figure 1 presents the collective results of the registered one-hour mass concentrations of the particular pollutants in the examined locations. For the conditions defined as a) and b), both in the rural and urban environment we could observe a small variability of the concentrations only for the case of SO_2. Greater variations in the level of the measured parameters were recorded for the unstable weather (a). Concurrently, with the exception of O_3 and NO_2, a two times greater value of the median for the remaining compounds was noted for the stable weather (b). The *ad oculos* observations revealed that in the rural areas, during the two days corresponding to the duration of the reported measurement, individual heat sources (and, hence, point sources of the emissions) were exploited to a similar degree. The above statement confirms that the depreciation of air

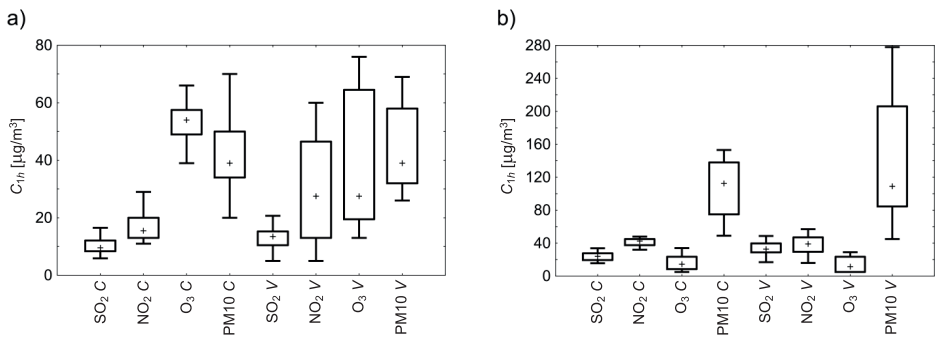

Fig. 1. Collective results of the registered one-hour mass concentrations, C_{1h} of the particular pollutants in the examined locations (C – city; V – village) for weather conditions a) and b). Boxes show the range between the 25th and 75th percentiles. The whiskers extend from the edge of the box to the 5th and 95th percentile of the data. The cross inside indicates the median value

quality is considerably correlated with the temperature drop, decrease of horizontal movement of air masses and increase and stabilization of the atmospheric pressure. The values of these parameters directly affect the effectiveness of the dispersion of pollutants in the troposphere. Concurrently, thermal conditions regulate the frequency and intensity of the use of the domestic heating systems. The position of the medians can indicate that with the exception for ozone, the greater values of the mass concentration of the examined core air pollutants were registered in the rural areas. This is probably due to the direct impact of the point emission sources in the vicinity. The mass concentration of PM10 is characterized by the greatest degree of variability in both measurement sites. Concurrently, only the concentration of the aerosol with the fraction below 10 micrometers exceeded the admissible levels (in the condition defined as (b)).

Table 1 presents the mean frequency of the occurrence of the particular classes corresponding to the general index and the sub-indices for the measured core air pollutants. As we can note, for the condition defined as (a), the sub-indices responsible for the gaseous pollutants are contained in the first (very low) and the second (low) classes, which means that the registered air pollution was small. In the long-term, for the case of the rural area, despite the very low and low values of the indices for SO_2, NO_2 and O_3, we cannot conclude that the air quality is overall satisfactory. Throughout nearly 40% of the periods corresponding to hourly results of registrations, the pollution assumes the value at the average level. In accordance with the CAQI index, this means that the air quality in the two measurement sites can be considered as similar. The detailed analysis of the hourly variations in the pollutant levels demonstrates that the PM10 formed the dominant pollutant (as it corresponded to 87% and 94% of total pollutant levels in the urban and rural areas, respectively). In the measurement spot located in Opole, despite the heavy traffic on the nearby ring road and local roads in the residential district (forming potentially the principal source of NO_2 emission in the analyzed town part), nitrogen oxide did not form the principal pollutant in any of the analyzed periods. This can also mean that the measurement sites was located too far from the main traffic arteries and the NO_2 concentration was diluted because of the horizontal movement of air masses. This result seems to confirm the conclusion stated by the Voivodeship Inspectorate of Environmental Protection that the most direct problem in Opole is associated with the pollution caused by particulate matter and this condition is regardless of the weather. Ozone was the dominant pollutant in the town throughout the four noon hours. This is quite standard for the effect and times when photochemical changes occur following the increased emission of nitrogen oxides accompanying its direct exposition to sun. For the case of the rural area, PM10 was the dominant pollutant recorded over 22 hours during the day. During the remaining 2 hours, it was not possible to identify the dominant source of pollution.

For the weather described by condition defined as B, in the urban areas we can observe average and high class of pollution. Despite the adverse conditions, and lack of states described as unstable atmosphere, the condition of very high air pollution did not occur during the experiment. This is likely to be due to the lack of the direct emission sources in the direct vicinity of the monitoring station. At the same time, the occurrence

Table 1

Frequency [%] of the occurrence of the index and sub-index classes (hourly data)

Index class	City					Village				
	Overall index	SO_2	NO_2	O_3	PM10	Overall index	SO_2	NO_2	O_3	PM10
Weather conditions “a”										
0–25	0.10	1.00	1.00	0.88	0	0.03	1.00	0.75	0.71	0
26–50	0.65	0	0	0.12	0.75	0.60	0	0.25	0.29	0.62
51–75	0.25	0	0	0	0.25	0.37	0	0	0	0.38
7–100	0	0	0	0	0	0	0	0	0	0
> 100	0	0	0	0	0	0	0	0	0	0
Weather conditions “b”										
0–25	0.08	1.00	0.88	1.00	0	0.05	1.00	0.87	1.00	0
26–50	0.05	0	0.12	0	0.04	0.02	0	0.13	0	0
51–75	0.31	0	0	0	0.33	0.22	0	0	0	0.29
7–100	0.56	0	0	0	0.63	0.38	0	0	0	0.38
> 100	0	0	0	0	0	0.33	0	0	0	0.33

Air quality index classes indication: 0–25 very low; 26–50 low; 51–75 medium; 76–100 high; > 100 very high.

of temperature inversion accompanied by a concurrent limitation of the exchange of air masses over the urban area has led to adverse aerosanitary conditions even in the urban area with high-rise building development. In this case, the principal source of pollution was associated with the local traffic. Nevertheless, the dominant pollutants did not include other substances than particulate matter. The greater distance from the stationary sources of fuel combustion for useful energy production also most likely has led to the fact that lowest class of air quality in this area did not occur. Such circumstances could not be avoided in the rural area, where the air quality was very poor throughout one third of the duration of the experiment. Again, very low and low sub-indices of air quality with regard to gaseous pollutants did not influence the overall air quality. The overall CAQI index broken down to the classes was considerable distinct from the result that was obtained in the urban area. The analysis of hourly variations in the concentrations of the particular substances demonstrates that PM10 was the only dominant pollutant. The considerably more adverse situation in the area of the compact rural development was associated with the excessive aerosol concentrations particularly in the afternoon and evening hours. Such circumstances directly result from the effect of the meteorological condition and common application of obsolete facilities as sources of heat production for households. The differences could not be explained in terms of the differences in the climate conditions, as it is often explained during the comparison of the CAQI indices for various towns around Europe [18].

Table 2 presents the results of the Spearman correlation for the particular pollutants corresponding to the two sites and meteorological conditions.

Table 2

Spearman correlation. *Rho* values. Results with bold fonts are statistically significant with $p < 0.05$. Italic fonts indicate data for village

Parameter	SO_2	NO_2	O_3	PM10
Weather conditions “a”				
SO_2		**0.36**	–0.33	**0.41**
NO_2	***0.77***		–0.28	–0.03
O_3	*–0.38*	*–0.15*		**–0.38**
PM10	***0.80***	***0.58***	*–0.23*	
Weather conditions “b”				
SO_2		**0.44**	–0.25	**0.47**
NO_2	***0.55***		–0.17	0.24
O_3	*0.32*	*–0.22*		**–0.35**
PM10	***0.83***	***0.73***	*–0.22*	

For all analyzed pollutants, statistically valid relations were observed between the variables nearly in the same list. Only for the urban area, the correlation index took on significant values for the relation between O_3 and PM10. Nevertheless, in accordance with the Guillford scale, the relation that was established is weak. The lack of

a considerable relation between the concentration of ozone and its main precursor (NO_2) results from the delay in the increase of ozone concentration originating from the physicochemical transformations of carbon monoxide. The considerable negative correlation between the ozone and PM10 is likely to be due to the different hours when the concentrations of the two compounds occur and it seems to be rather coincidental. The forecasted and very strong positive relation between particulate matter and sulphur dioxide occurred for both meteorological conditions in the rural area. This relation is also more visible in the rural than in the urban area, and it demonstrates the characteristic of significance as well. This result confirms the commentary to the results from Table 1 and expressly indicates that the heating systems in the rural areas use low quality fuel which are enriched with sulphur. The relation between the mass concentrations of NO_2 and SO_2 as well as NO_2 and PM10 in the two sites prove to be significant, and we can note that for the results in the rural area, we can note the impact of the point emission sources from domestic boilers. Besides, weather conditions (*ie* greater values of *rho* for the condition defined as "b") have an influence on the value of the correlation coefficient.

It is interesting to note the mutual relations between the same types of pollutants measured concurrently in the urban and rural area. Statistically relevant Spearman correlations were only established for the case of PM10 (–0.64 and –0.54, for the conditions defined as "a" and "b", respectively). At the same time, during the unstable weather (a), a considerable positive relation was established for the nitrogen dioxide concentrations. The normalized profiles developed in accordance with the formula (1) for hourly concentrations of the pollutants and the particular locations and conditions confirm the results of the correlations (Fig. 2).

As for the fluctuations in the mass concentration of NO_2 for the conditions defined as (a), we can observe the occurrence of two maximums. For the case of the urban area, this is predominantly attributable to the increased traffic (corresponding to the morning and afternoon rush hours). For the rural area, the reason is associated with the periods corresponding to the intensive use of the domestic boilers. The calculated correlation coefficient confirms the results of the graphical interpretation. For the urban area, during the stable weather conditions (b), the profile of the distribution of the hourly NO_2 concentrations does not bear resemblance to the profile in the rural area. In the latter case, we can only observe an afternoon-evening peak, and the morning increase in the concentrations is characterized by a further stabilization, which also corresponds with the meteorological conditions, however, it is not compatible with the further sudden increase. For the rural area, we can observe a similar profile to the one that was observed for the conditions in (a).

With regard to the profiles of the mass concentrations of ozone, in particular for the urban area, we can observe a delay in the occurrence of the lowest values of the concentrations in relation to the ozone precursor, namely NO_2. Regardless of the weather, the highest concentrations are recorded in both measurement sites around the noon. Particularly high concentrations in the town are noted after dusk (a), which can mean that the conditions in the troposphere tend to remain constant due to the lack of forces enabling the atmosphere to get rid or reduce the impact of the derivative

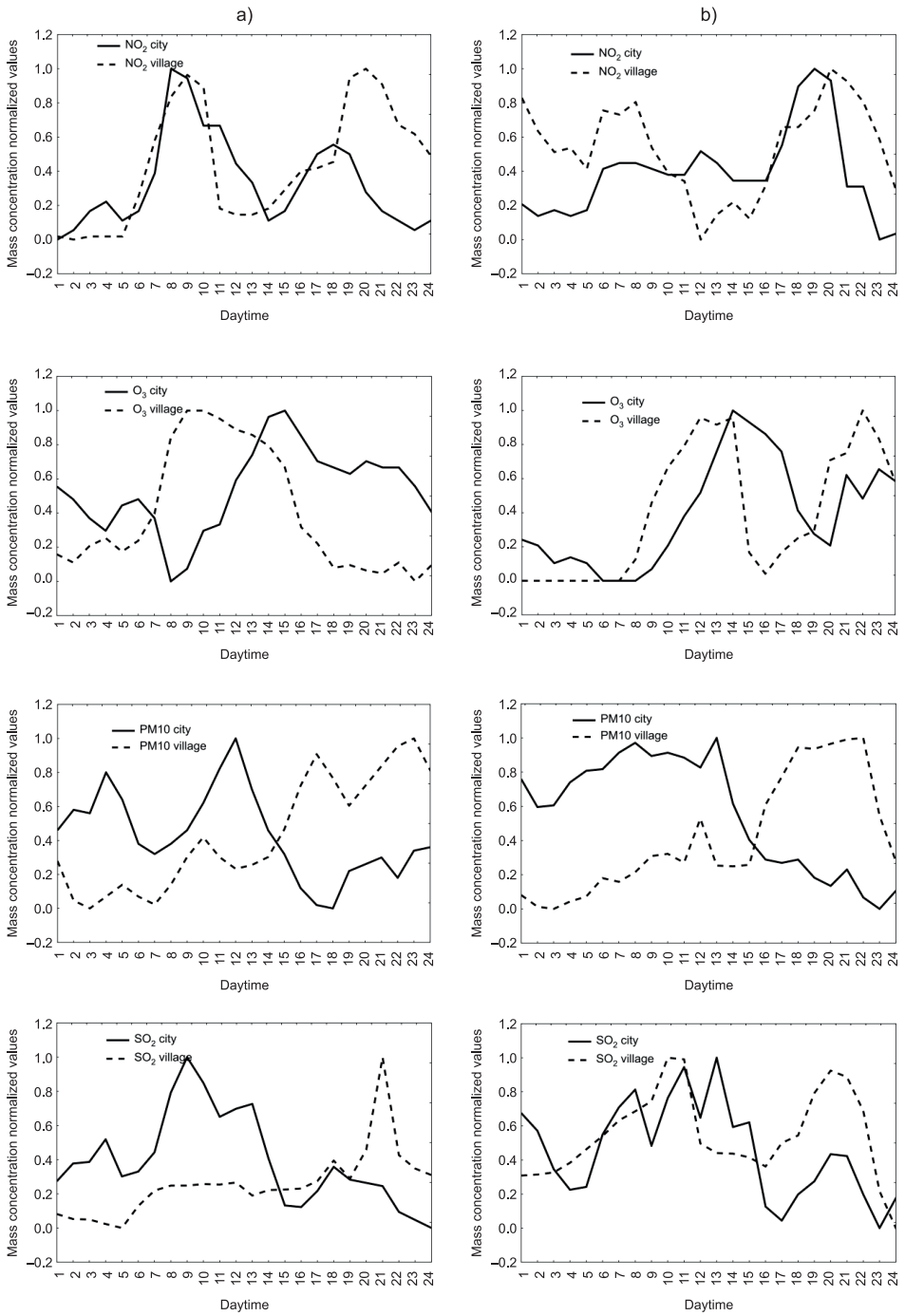

Fig 2. Core pollutants profiles for a) and b). Weather conditions (hourly data)

compounds. The evening and night increases in the ozone concentrations, which are followed by subsequent maximums in both areas for the condition defined as (b) are difficult to interpret, in particular in the context of the occurrence of the stable conditions in the ground level troposphere.

It is equally difficult to explain the profile of the hourly variations in the aerosol concentrations in the urban area accompanying the condition defined as (b). A sharp, evening drop in the concentration of PM10 in Opole was also confirmed the results of the air quality monitoring registered by another Voivodeship Inspectorate of Environmental Protection station located at the distance of 4 km from the one used in this study [19]. The above fact suggests that equipment error as well as non-specific short-term changes in the parameters of the ground troposphere are out of the question. In turn, adequate interpretation is made difficult.

The drop in the PM10 concentration in the town (during the condition defined as "a") could be justified by the action of the wind and minimization of the impact of the emission sources in its close vicinity. Concurrently, the increase in the concentration of aerosol in the rural area was determined by the more intensive exploitation of domestic boilers resulting from the temperature drop in the evening, which is confirmed by the registrations made in the vicinity of the measuring equipment. The evident differences in the profiles of aerosol concentrations in both sites are revealed in the values of the Spearman correlation coefficient.

For the case of the profiles representing the variations in SO_2 concentrations, we can note differences between the rural and urban areas. For the case of the former, despite the statistically insignificant correlations, we can conclude that the hourly variations in the concentration of sulphur dioxide are similar to the profiles for PM10, which confirm the impact of the principal source which determines the air quality in the rural area. As for the town, we can observe considerable fluctuations, in particular at the times corresponding to the occurrence of the stable weather (b). The nominal values of the SO_2 concentrations are relatively small in comparison to the concentrations of the remaining pollutants (which is confirmed by the CAQI sub-index). This, in turn, can have an impact on the variations of the normalized values that were demonstrated by the profile.

The ultimate verification of the similarity of the mass concentrations of the core pollutants in the tested sites involved the verification of the research hypotheses stated at the beginning. Both hypotheses were verified by the application of the Wilcoxon's signed-rank test. As a consequence, it was found that both in the urban and rural areas, the concentrations of the compared pairs of identical pollutants determined during diverse weather conditions were statistically different. In none of the cases, we could establish the exceeding of the level of the test relevance ($p < 0.001$). Hence, the hypothesis stating that *during winter accompanied by a variety of weather conditions, the hourly variations of the parameters characterizing air quality in a given area do not reveal statistically relevant fluctuations along the 24-hour period* has to be definitely rejected.

The Wilcoxon's signed-rank test demonstrated that during the weather conditions described by the unstable conditions of the ground-level troposphere (A), the hourly

mass concentrations of SO_2 and PM10 measured in the urban and rural areas did not reveal statistically significant differences ($p = 0.051$ and $p = 0.484$, respectively). However, statistically significant differences were registered for the case of NO_2 and O_3 ($p < 0.01$). During the weather conditions described by the stable ground-level troposphere (B), statistically significant results were established only for SO_2 ($p < 0.01$) with regard to one-hour mass concentrations. For the remaining pollutants, statistically significant results were not found ($p = 0.057$ for NO_2, $p = 0.654$ for O_3 and $p = 0.383$ for PM10). The result of this test indicated that the verified hypothesis that *during the winter, for identical weather conditions, the degree of urban development do not affect the variability profile of the on-hour values of the parameters characterizing the air quality* can be considered as true only to a limited extent.

Conclusions

The comparison of aerosanitary conditions in two and more locations performed by means of the CAQI index always forms a suitable solution. The results of a comparison of indices and sub-indices are similar to the classical approach conducted with the aim of verification, such as statistical analysis. The summary of CAQI data enables the researchers to study the potential changes in the ratios of the particular emission sources in a given area.

In the cold season, during the occurrence of the stable weather in the urban and rural areas, the levels of the pollutants in the immission phase are primarily affected by the local emission sources. We can assume that the results gained in the residential areas in towns and areas of compact rural development will be representative for a wide range of applications, primarily due to the similar pattern of useful energy consumption in the households (district heating in the urban and domestic boilers in the rural areas). The short-term variability of the aerosanitary air quality is strictly linked to the weather conditions, determined mainly by the pressure, temperature and direction and speed of air masses. The compared values registered during 24-hour profiles of the principal air pollutant indicate that the degree of urban development of the residential areas does not have a decisive impact on the characteristic and course of these profiles. For both observation spots it was observed that aerosol forms the dominant pollution determining the air quality in the examined areas.

The conditions of the air quality in winter, expressed by the one-hour tests, were found to be similar in the rural areas with compact development and in the vicinity of the greater and more populated residential district in the urban area (despite the fact that the latter is free of the individual sources of pollutant emissions associated with energy production from fuels). For the case of severe bad weather (in which dispersion of pollutants is limited and causing the more intensive use of the domestic boilers), the air quality in the rural areas was proved to be worse than in the nearby town. The similarity in terms of the characteristics of the use of individual heat sources in the households located in the rural areas in Poland leads to the statement that the above conclusion is true for a wider population.

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JAKOŚĆ POWIETRZA DLA ODMIENNYCH WARUNKÓW POGODOWYCH W DWÓCH MIEJSCACH OBSERWACJI

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Abstrakt: Artykuł przedstawia wyniki krótkoterminowych badań nad zmiennością jakości powietrza dla odmiennych warunków pogodowych w dwóch, różniących się stopniem zurbanizowania i sposobem użytkowania, miejscach obserwacji. Projekt badawczy przeprowadzono na obszarze osiedli mieszkalnych w mieście i na wsi w sezonie chłodnym. Przeanalizowano 384 niezależnych, 60-minutowych rejestracji wartości stężenia podstawowych zanieczyszczeń powietrza (NO_2, SO_2, O_3 i PM10). Wykorzystano referencyjne metodyki pomiarów wielkości fizycznych. Rezultaty rejestracji porównano przy wykorzystaniu ogólnego indeksu jakości powietrza (CAQI) a następnie przeanalizowano i zweryfikowano przy użyciu testów nieparametrycznych (korelacji Spearmana i testu Wilcoxona). Stwierdzono, że porównywanie jakościowych parametrów powietrza w różnych lokalizacjach przy użyciu CAQI jest dobrym rozwiązaniem. Wykazano, że krótkotrwała zmienność aerosanitarnej jakości powietrza jest ściśle związana z panującymi warunkami pogodowymi. Stwierdzono, że w sezonie zimowym, stopień zurbanizowania terenów zamieszkałych nie ma decydującego wpływu na dobowy kształt profili stężeń podstawowych zanieczyszczeń. Wykazano, że zanieczyszczeniem ustalającym ogólną jakość powietrza jest PM10. Znaleziono, że w okresie chłodnym, jakość powietrza na zamieszkałych obszarach wsi nie jest lepsza niż na znacznie bardziej ludnym osiedlu miejskim.

Słowa kluczowe: zima; miasto; wieś; jakość powietrza; zanieczyszczenia wskaźnikowe, NO_2, SO_2, O_3, PM10

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THE EFFECTIVENESS OF VARIOUS TYPES OF VENTILATION ON AIR QUALITY IN MULTI-FAMILY BUILDINGS

SKUTECZNOŚĆ RÓŻNYCH TYPÓW WENTYLACJI NA JAKOŚĆ POWIETRZA W BUDYNKACH WIELORODZINNYCH

Abstract: Currently, regulations and norms require control of building ventilation only in terms of air velocity, which unfortunately does not always guarantee the ideal air quality required for health reasons. The study investigates the effectiveness of various types of ventilation in multi-family residential buildings (buildings occupied by more than one family) with particular emphasis on natural ventilation, which is the most common solution in residential buildings in Poland. The effectiveness of ventilation systems and their influence on basic properties of air quality, *ie* carbon dioxide concentration, relative humidity and temperature were examined, as well as the possibilities of changing the work done by ventilation systems in multi-family residences to adjust factors pertaining to air quality. The results obtained from the research show that, in the case of multi-family residential buildings, natural ventilation does not function effectively and should be replaced by mechanical ventilation – preferably intake and exhaust ventilation with heat recovery.

Keywords: ventilation system, multi-family buildings, air quality, carbon dioxide concentration, air humidity

Introduction

The quality of indoor air in which people live depends on the type of rooms and the way they are used. In residential buildings, pollution that decreases air quality results mainly from human life functions. Carbon dioxide contamination is caused by the process of breathing (people exhale carbon dioxide) but also during the combustion process in gas stoves, gas water heaters or biomass fireplaces. An important factor influencing indoor air quality is water vapor produced in bathrooms and kitchens and emitted from the surface of the skin and the exhaled air [1–3].

In most residential buildings, the aforementioned air quality deteriorating factors cannot be completely eliminated. Therefore, after a few hours of occupancy in a closed

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room, the recommended by the European division of World Health Organization – WHO CO_2 concentration limit of 1000 ppm can be exceeded [4–6]. A person spends at least 1/3 of his life inside the house or flat, therefore, the only way to ensure adequate air quality in residential spaces is to replace the air with a well-functioning ventilation system that channels exhaust air and introduces fresh air from the building's environment to the living space.

In Poland, the parameters of indoor air quality in residential buildings are specified in the Polish PN-B-03430:1983/Az3:2000 Standard: Ventilation in public housing and public buildings – Requirements [7]. According to the aforementioned standard, air parameters affecting the comfort of indoor climate are: air temperature, air humidity, physical and biological quality of air and CO_2 concentration. According to [7] the apartment ventilation system should provide at least:

a) supply of outdoor air to living rooms and kitchens with outside windows;

b) removal of exhausted air from the kitchen, bathroom, separate toilet, and auxiliary room with no window (closet, dressing room) [7].

In order to be able to compare the efficiency of various ventilation systems for residential spaces, it is necessary to determine measurable flow parameters such as local velocity and temperature of air distribution, pollution concentration distributions, etc., characterizing the essential features of air distribution and its target effects and performance [8]. Taking into account the above, it was decided to conduct research to determine the efficiency of various ventilation systems for multi-family residential buildings, with particular regard to natural ventilation. The selection of research facilities equipped with natural ventilation systems results from the fact that this ventilation system is the most common solution in multi-family residential buildings in Poland.

Materials and methods

Two research facilities were selected to compare the efficiency of natural ventilation systems in different multi-family buildings. Object 1 is a residential area of 56 m^2, located on the 3rd storey in a 11-storey multi-family building, built in the technology of a large plate. Object 2 is a residential building of 60.0 m^2, located on the 3rd storey in a 4-storey building, built in the traditional technology. There are two people living in both houses, which, taking similar area of objects into account, will allow to compare the results of the research. The layouts of both objects are shown in Fig. 1.

The studied objects are equipped with a ductile natural ventilation system. In buildings up to 25 m (7 storeys) above ground level, gravity or mechanical ventilation can be used. For buildings above 25 m, only mechanical ventilation should be used. The dwelling chosen as object 1, despite being higher than 25 m, has not been equipped with mechanical ventilation. This is due to the fact that it was built in the 1970s when the standards that were in force at that time allowed natural ventilation for such high buildings.

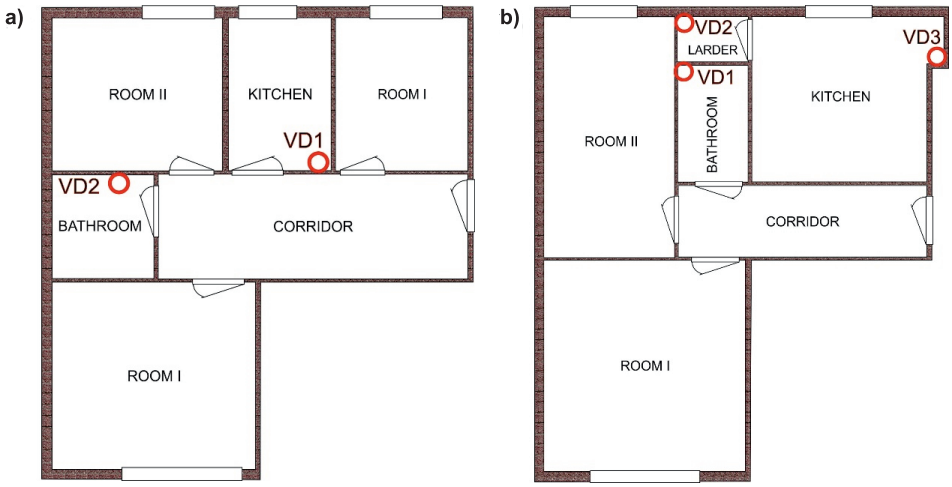

Fig. 1. Floor plans of facilities: a) apartment 1, b) apartment 2. VD – ventilation ducts

The scope of the research included:

– studying the performance of the gravitational ventilation system of the objects during the heating season, as well as after the heating season, by measuring the air flow for the whole object's area;

– investigation of the effect of changes in the air flow rate on the concentration of carbon dioxide and relative humidity in the object.

In buildings equipped with a natural ventilation system, exhaust air is discharged from kitchens, bathrooms, toilets, and auxiliary rooms with no windows through the exhaust holes located in the upper part of a wall and connected to the vertical gravity ventilation ducts. Object 1 contains two ventilation ducts. Channel inlets are located in the bathroom and the kitchen (location of inlets in individual rooms is shown in Figure 1a). In contrast, there are 3 channels of gravity ventilation in Object 2. Ventilation inlets are located in the bathroom, the pantry and the kitchen (Fig. 1b).

The ventilation air flow in the analyzed objects was determined by summing ventilation air flows for inlets to all ventilation ducts in the given objects. The air flows in the individual ventilation ducts were calculated on the basis of the air velocity in the individual inlets of the ventilation ducts. A Kestrel 2000 anemometer with a resolution of 0.1 m/s and accuracy of ± 3% was used for speed measurement. At the same time, measurements of indoor air temperature (T_w) and outdoor temperature (T_z) were performed. The relative humidity of indoor air was also recorded (±), as well as atmospheric pressure (p). These measurements were made using the Commeter C4130 hytherograph, which measures temperature to the nearest 0.4^{o}C, relative humidity to the nearest ± 2.5% and atmospheric pressure to the nearest ± 2 hPa. The main parameter determining the efficiency of the ventilation system, for the purpose of the research, was the concentration of carbon dioxide, recorded in all the rooms of analyzed objects. It is a widely used method for analysis of ventilation systems, adopted by many researchers

[9–13]. Measuring of carbon dioxide concentration was made at three measuring points in each room using AZ 77535 multifunctional carbon dioxide gauge with accuracy of 30 ppm ± 5% of reading. On the basis of obtained results,, the approximate carbon dioxide concentration for the whole area of objects was calculated.

The study of the ventilation system and air parameters in analyzed objects was conducted between September 2015 and May 2017, *ie* during and after the heating season.

All indoor air quality tests were performed at different heights and at different locations in individual rooms and then average values were determined. The same test procedure was used for both objects. Measurements were carried out in five-day cycles, continuously recording carbon dioxide concentrations, while remaining air parameters were measured every 15 minutes 24 hours a day. The study was conducted only on working days when the daily cycle of residents' activities was almost identical. This approach allowed to compare the results obtained at different times of the year and with different weather conditions.

Results and discussion

For both research facilities located at various points in Opole, outdoor air parameters were recorded. The analysis of the obtained results showed that the background of CO_2 in the outdoor air reaches an average value of 540 ppm. When it comes to temperature, its average monthly values correspond to the values given in the Polish climate database compiled by IMGW for the meteorological station of Opole [17].

The examples of variation of carbon dioxide concentration in the examined objects during the heating season and summer season are shown in Fig. 2.

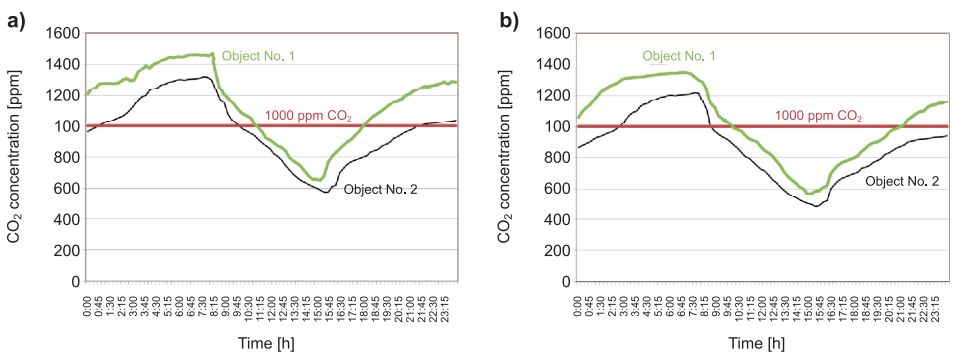

Fig. 2. Selected CO_2 concentration variation during: a) the heating season, b) summer season

The examples of variation of the ventilation flow in examined objects are shown in Fig. 3.

The analysis of the data presented in Fig. 3 shows that in both analyzed objects natural ventilation systems do not meet the requirements of the Polish PN-B-03430:1983/Az3:2000 Standard [7] for the required air exchange rate. It should also be noted that, after the

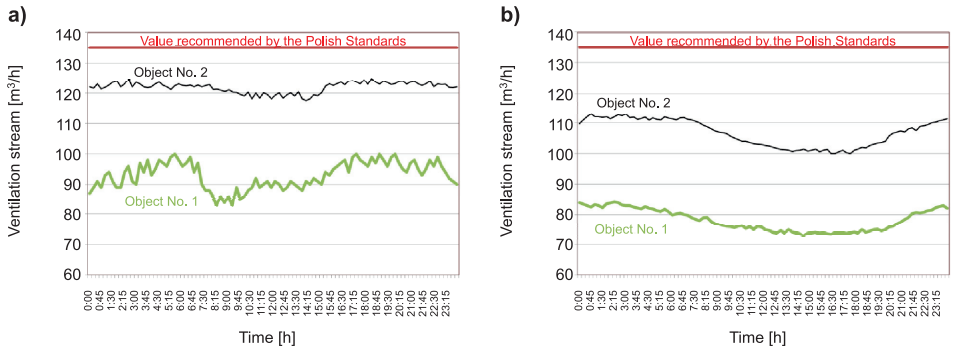

Fig. 3. Selected ventilation stream variation during: a) the heating season, b) summer season

heating season, in the case of both surveyed objects, the ventilation air flow is clearly reduced. During the heating season, both objects were periodically ventilated by opening the windows, but due to the reduction of the air flow, no significant reduction in carbon dioxide concentrations was observed in the surveyed objects (Fig. 2).

The examples of relative atmospheric humidity in the examined objects are shown in Fig. 4.

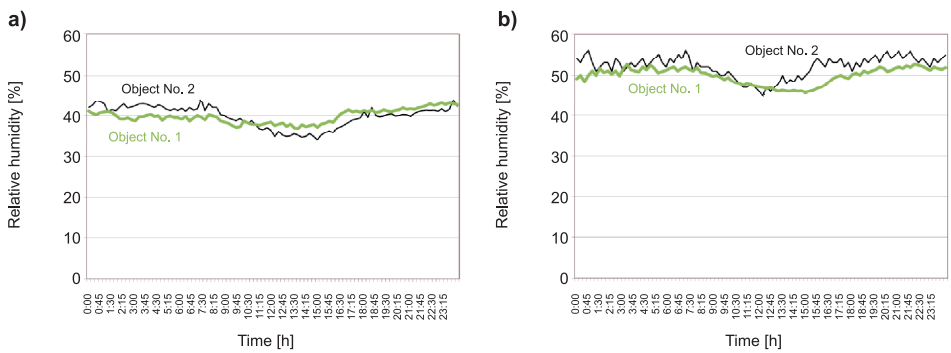

Fig. 4. Selected relative humidity variation: a) during the heating season, b) summer season

The measurements of carbon dioxide concentrations during night hours (22:00–6:00) were also conducted in the room where the occupants slept. The values of carbon dioxide concentration depending on the way of the room ventilation in a given objects are presented in Table 1.

On the basis of the obtained research results it was estimated that a person staying in the analysed object is the source of an average of 11.5 dm^3 of carbon dioxide per hour. This value is variable and highly dependent on the type of physical activity (there were clear differences between hours of sleep and hours of greater physical activity of the occupants). The value of the average CO_2 emission for a single occupant of the object allowed to determine the optimal multiplicity of air exchange in the object performed by the ventilation system.

Table 1

Maximum carbon dioxide concentration in the rooms in which the occupants slept, with different methods of ventilating the room

Way of the room ventilation	Maximum carbon dioxide concentration [ppm]	
	Object 1	Object 2
Closed window and door (during the heating season)	4750	4460
Open door (during the heating season)	1540	1320
Closed door and micro ventilation through the window (summer season)	1670	1250
Open door and micro ventilation through the window (summer season)	1000	920

The tests of indoor air parameters in both research objects showed that despite the natural ventilation system used in accordance with the requirements of Polish PN-03430:1983/Az3:2000 Standard, after 3 hours of continuous occupancy, the concentration of carbon dioxide exceeded the recommended value of the European division of World Health Organization (WHO), which is 1000 ppm [4, 5]. On the other hand, the relative humidity value of the air, even though the number of occupants in the object increased, did not reach the recommended value, *ie* 50–60%.

Less effective operation of the natural ventilation system has been observed in the object 1. In the case of an 11-storey building, natural ventilation does not provide air exchange required by the Polish Standard for individual premises. For both research facilities, the efficiency of the natural ventilation system has been much lower after the heating season, but this can be significantly improved by regular ventilation of the premises. When outdoor air temperatures exceed 20^{o}C, additional intensive ventilation will not cause thermal discomfort to residents.

Based on the carbon dioxide emission factor determined during the test and the optimal multiplicity of air exchange in the object of 0.5 h^{-1}, the performance, fan-working period and cross-sections of wall ventilators can be chosen in such a way as to ensure optimal air exchange to obtain indoor climate recommended by the Polish Standard [6].

When planning a thermal efficiency improvement of a tall multi-family building such as the object 1, it is worth considering changing the existing natural ventilation system to individual ventilation of the flats with heat recovery system by means of recuperators. The wall recuperator is a heat exchanger with fresh air flow through the building's wall separately for each room (Fig. 5). In the wall recuperator, the used warmed up air is thrown out of the room and heats up the ceramic element. Then the device changes the direction of air flow and fresh air is drawn from the building's surroundings into the room and heated by the heat stored in the ceramic element. The use of this type of wall recuperators in all the rooms allows to recover up to 85% of the heat from the air evacuated from the dwelling to the environment compared to the current ventilation system of the objects under test. The use of a wall recuperator in a room where the occupants sleep will keep the optimal concentration of carbon dioxide

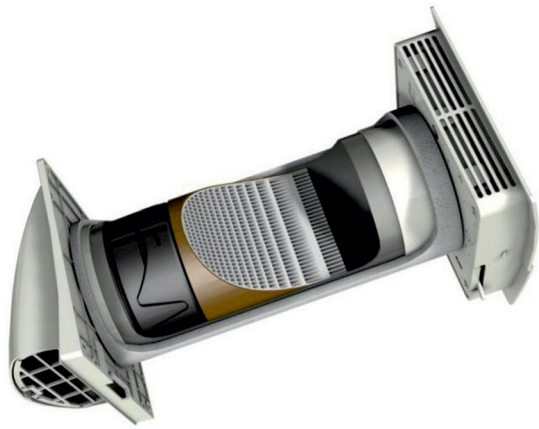

Fig. 5. Scheme of the heat recovery inside wall [18]

while ensuring thermal comfort and reducing heat loss from the building. Installation of the centralized mechanical ventilation with heat recovery in such a large facility is technically very difficult to implement, however, by installing separate ventilation systems for every flat, equipped with wall recuperators, the modernization of the ventilation system can be done without major renovations of the entire building.

Conclusions

The results of the studies show that the natural ventilation systems of multi-family buildings do not fulfill their role. The lack of opportunity to regulate ventilation air flow, limited fresh air flow (during the heating season, resulting from the tight closing of the premises to minimize heat loss), and the use of gas cookers reduces the supply of oxygen to the living space. This results in a rapid increase of carbon dioxide concentration in the air and adversely affects the microclimate of the premises and the well-being of the residents.

Based on the results of the study, it was calculated that each person staying in the analyzed object is the source of carbon dioxide emission of 11.5 dm^3 per hour. Established during the tests the optimal multiplicity of air exchange in the object is 0.5 h^{-1}.

The installation of additional wall ventilators allows for an increase in the supply of fresh air to the premises, but significantly reduces the thermal comfort of the rooms and causes significant heat loss. For the analyzed objects, the most advantageous solution is to change the existing natural ventilation system to individual ventilation system with heat recovery by means of wall recuperators. The results of the research also indicate the need to make changes in construction legislation, forcing the owners of existing multi-family buildings to change natural ventilation systems to mechanical ventilation systems, preferably with heat recovery means.

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SKUTECZNOŚĆ RÓŻNYCH TYPÓW WENTYLACJI NA JAKOŚĆ POWIETRZA W BUDYNKACH WIELORODZINNYCH

Samodzielna Katedra Inżynierii Procesowej
Uniwersytet Opolski

Abstrakt: Przepisy prawne oraz normy obligują do kontroli systemów wentylacji budynków jedynie pod względem prędkości strumienia powietrza, co niestety nie zawsze gwarantuje zalecaną ze względów zdrowotnych jakość powietrza. W pracy podjęto badania skuteczności różnych typów wentylacji wielorodzinnych budynków mieszkalnych ze szczególnym uwzględnieniem wentylacji naturalnej, stanowiącej najczęściej spotykane rozwiązanie w budynkach mieszkalnych w Polsce. Badano wpływ skuteczności wentylacji na podstawowe parametry charakteryzujące jakość powietrza, tj. stężenie ditlenku węgla, wilgotność względną oraz temperaturą. Badano również możliwość regulacji pracy systemu wentylacji budynków wielorodzinnych w zależności od zmieniających się parametrów jakości powietrza. Wyniki przeprowadzonych badań wykazały, iż w przypadku wielorodzinnych budynków mieszkalnych systemy wentylacji naturalnej nie spełniają swojej funkcji i powinny zostać zastąpione przez systemy wentylacji mechanicznej (najlepiej nawiewno-wywiewne z odzyskiem ciepła).

Słowa kluczowe: system wentylacji, budynki wielorodzinne, jakość powietrza, stężenie ditlenku węgla, wilgotność powietrza

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RAINWATER POTENTIAL USE IN DORMITORY BUILDING: DRINKING WATER SAVINGS AND ECONOMIC COSTS

MOŻLIWOŚCI WYKORZYSTANIA WODY DESZCZOWEJ W DOMU STUDENCKIM: OSZCZĘDNOŚĆ WODY PITNEJ I KORZYŚCI FINANSOWE

Abstract: Climate change, improper use of water resources, surface waters pollution as well as increase of water requirements are the results of growing population of people in the world. It causes that the most countries, including Poland, are faced with the deficit of water. Because of this a variety of measures are taken continuously in order to reduce the depletion of the global water resources, eg using rainwater in toilet flushing, car washing, washing machines, irrigation of arable land or watering green areas. The use of this type of solutions may also decrease fees charged for water supply to buildings which often constitute a substantial part of their upkeep expenses. In this paper, the financial effectiveness of the use of the rainwater harvesting system (*RWHS*) for toilet flushing is presented. The analysis was conducted using a simulation model and as a subject of study a dwelling-house (a dormitory) located in Poland was chosen. The study also analyzed the influence of a retention tank size on efficiency of the economic use of rainwater utilization system for the dormitory. In the financial analysis two financial ratios were determined: the Net Present Value (*NPV*) and the Discounted Payback Period (*DPP*), and sensitivity studies were conducted as well. The conducted analysis demonstrated that the use of the *RWHS* system in the analyzed building is cost-effective and that it may reduce water requirement for toilet flushing by 11 to 22%, depending on the capacity of the retention tank.

Keywords: rainwater harvesting system, rainwater management, drinking water savings, financial analysis

Introduction

The water resources of our planet are huge and could theoretically satisfy the needs of the Earth's entire population; however, their non-uniform distribution and irrational water management by humankind mean that in many countries the supply of this

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resource is an immense problem. More than 97.4% of the Earth water resources are sea and ocean waters which, due to their salinity, are not fit for use by humankind. The remaining 2.6% of it is fresh water which in substantial part is entrapped in glaciers and snow cover. Only an insignificant part of these resources, equaling 0.6%, is fresh water which can be used as a source of potable water.

The current annual demand for fresh water all over the globe is about 4500 km^3, while the spatial diversification of the ≤ale of needs does not coincide with the distribution and availability of water resources, and causes water deficits in many countries. Moreover, according to some scenarios of economic growth, the annual demand for fresh water will increase to 6900 km^3 in 2030 and may lead to a shortage of 40% in the total global water supply [1]. The water deficit is most painfully felt by the countries of the North and Central Africa, South America and Mid Asia. However, many European countries, including Poland, also have to deal with a water shortage.

According to the United Nations 783 million people all over the globe [2], including more than 120 million in Europe, have no access to a safe source of potable water [3], and every year due to this lack or diseases caused by consumption of bad quality water almost 3.5 million of people die [4], including nearly 1.5 million children [5].

Numerous prognoses also show that in the coming decades global water resources will shrink while the demand for it will increase dramatically. Climate changes, an increasing demand for food (agriculture's water requirement is 70% of the global demand [6]) and energy or the sanitary needs of continuously growing population are factors influencing the water crisis. A serious threat to shrinking water resources is also the improper use of water. Furthermore, urban development, which is the main driving force causing the global changes and environmental degradation, causes rapid depletion of environmental resources [7, 8]. Therefore, natural resource management, including water resources, should be sustainable [9].

Poland is one of the most water-deficient European countries and is ranked 26^{th} in Europe considering the quantity of water resources which are characterized by high seasonal fluctuations and a non-uniform territorial distribution. In Poland the per capita ratio of water resources is 1600 m^3/year while the European average per capita value is estimated at 4500 m^3/year [10]. Poland has not only less and less water but it is also heavy contaminated bacterially and physicochemically. To improve this situation, it is necessary to introduce a strategy of water management related among other things to new methods of using water resources.

One method for reducing use of water resources is the economic utilization of rainwater. Systems for collecting and using this water are also used in other countries. Depending on climate conditions and the type of building where the rainwater system is installed, a saving on the demand for tap water is obtainable at different levels. Rainwater harvesting systems (*RWHS*) are considered by researchers to be one of the strategies enabling the water management sector to adapt to a changing climate [11–13].

In Poland, as it happens in many highly industrialized countries, rainwater cannot be used for consumption purposes due to heavy air pollution and operative regulations, but it can successfully substitute tap water in toilet flushing, car washing, laundering, irrigation of cultivable land or watering green areas [14–20]. Most commonly, the

rainwater is used to flush toilets in residential buildings [21–24]. However, such installations are also utilized in large sporting facilities [25] and university facilities [26], in supermarkets [27] and office buildings [28, 29].

In the literature one can find a great deal of information on the calculation of the benefits, in particular financial profits, resulting from RWHS applications. Rahman et al. conducted a life cycle cost (*LCC*) analysis for three different tank volumes and three variants of rainwater use: (i) toilet and laundry (ii) irrigation and (iii) a combination of toilet, laundry and irrigation [30]. They ascertained that for all these cases the cost benefit ratios for a *RWHS* are less than 1. Only with government subsidy is it possible to gain a cost benefit ratio greater than 1.

Ghimire et al. conducted a *LCC* financial analysis of the utilization of rainwater harvesting systems for toilet flushing in industrial facilities. In addition, they also calculated the Net Present Value Benefits (*NPVB*) for these systems. On the basis of their findings, they discovered that *RWHSs* are not cost-effective for the analyzed buildings [31].

And then, Farreny et al. used a Life Cycle Cost analysis to define the total costs of rainwater retention and utilization systems in multi-family buildings in Spain; they analyzed two scenarios for tap water prices: current prices and the prices including a future increase in water buying costs. The findings demonstrate that *RWHSs* used in densely populated areas in a Mediterranean climate are only cost-effective on certain assumptions, *ie* the assumed tap water prices and increase in tap water prices [32].

In England, a financial analysis was conducted for 384 rainwater retention and utilization systems constructed in this country. A Life Cycle Cost methodology was employed for this purpose and different scenarios were taken into consideration for the future performance costs of these systems. In each case it was ascertained that rainwater harvesting was far less cost-effective than supplying the analyzed buildings with tap water alone [33].

The review of the published studies showed that in most cases the use of *RWHS* system is not financially viable, but it is an individual matter and depends on many factors, including the building location, climatic conditions, the technical parameters of the installation and the size of the surface from which rainwater is collected. For improving the financial effectiveness of the use of the *RWHS* system the subsidies from government may affect. An example of this can be research conducted by Gotur and Devendrappa in Karnataka, India, where the government covered more than 40% of the investment. The study of economic viability of investment in *RWHS* systems revealed that the Net Present Value was positive and Pay Back Period was very low [34].

In Poland, the economic use of rainwater utilization systems is rare. There is no detailed data concerning neither their performance nor designing guidelines which enable such systems to be designed in Polish conditions. The findings of analyses conducted on the potential utilization of these systems for residential housing have been presented, inter alia, in papers [35–37].

The subject of this paper is to determine the financial effectiveness of the rainwater harvesting system for toilet flushing in a residential building as well as the possible water savings examined in Polish conditions. For the study purposes, a dormitory

building was chosen where the rainwater harvesting system is planned for toilet flushing. The findings concerning the financial effectiveness of this investment may constitute valuable guidelines for an investor in the decision-making process.

Case study

The study of the possible economic use of rainwater was carried out for a facility located within the campus of the Rzeszow University of Technology in the city of Rzeszow, Poland. The city of Rzeszow is a provincial capital of 180 thousand inhabitants and an area of 116 km^2, which has a history dating back 656 years. The city is the biggest center of industry, commercial and service activities, as well as an academic and cultural center, in South-Eastern Poland (Fig. 1).

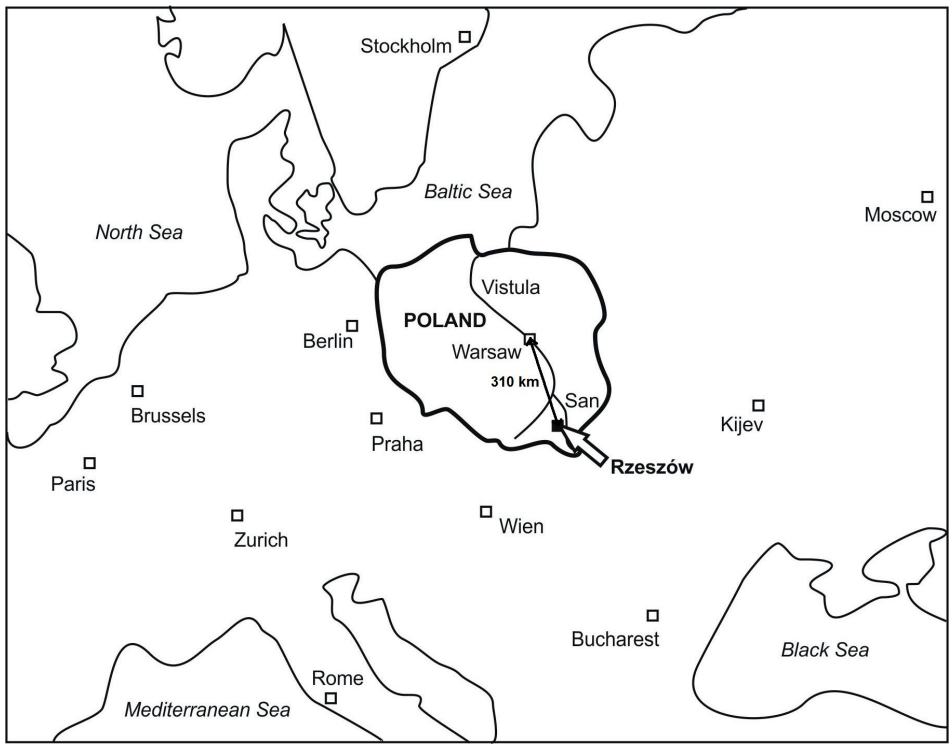

Fig. 1. Location of case study city in Poland

The campus of the Rzeszow University of Technology is located in the city center. On an area of forty thousand square meters there is a complex of seven dormitories which accommodate approximately two and a half thousand students. Because of the planned investment projects aimed at modernizing the water supply systems for the campus, which include the development of the economic use of rainwater, a cost--effectiveness study of *RWHS* in the "Ikar" dormitory was carried out. The university

dormitory location within the campus area is shown in Fig. 2. It is an eleven-storey building with a full basement, designed for 600 students.

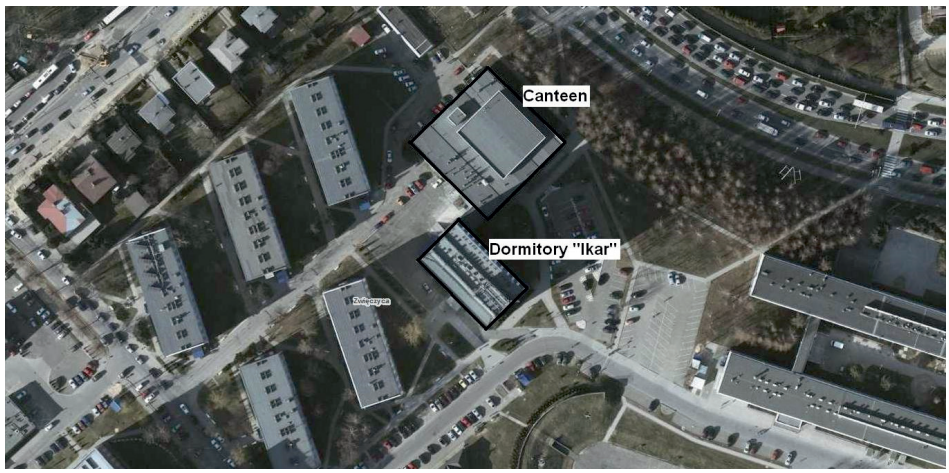

Fig. 2. Location of the analyzed dormitory within the campus area

For the dormitory, the analysis of the possible use of rainwater for toilet flushing was carried out together with a financial analysis of capital expenditure. It was assumed that the rainwater would be collected from the roof surface of the "Ikar" building and a neighboring canteen, and then the water would be drained via a piping system to an underground tank, located in the vicinity of the dormitory.

Method

To analyze the performance of the economic use of the rainwater utilization system at the chosen academic facility, a simulation model has been prepared, the algorithm for which is shown in Fig. 3. The elaborated model is versatile and can be used for a broad range of research. This model can be useful in the research on the *RWHS* performance in different types of buildings as well as for different locations and parameters of the system.

The functioning of the installation in formulated simulation model is described with the following conditions which determine the processes of rainwater flow, its accumulation and release of water to sanitary installation and sewers.

- Filling in and accumulation of rainwater in the tank:
  If $V_{rki} + V_{di+1} > V_z$ to $V_{i+1} = V_z$, $i = 1, 2, ..., n$
  If $V_{rki} + V_{di+1} \leq V_z$ to $V_{i+1} = V_{rki} + V_{di+1}$, $i = 1, 2, ..., n$
- Rainwater intake from the tanks by the installation:
  If $V_{rpi} - V_s < 0$ to $V_{rki} = 0$ and $V_{ui} = V_{rpi}$, $i = 1, 2, ..., n$
  If $V_{rpi} - V_s \geq 0$ to $V_{rki} = V_{rpi} - V_s$ and $V_{ui} = V_s$, $i = 1, 2, ..., n$

- Flow of mains water to the tank:
  If $V_{rpi} > V_s$ to $V_{wi} = 0$, $i = 1, 2, ..., n$
  If $V_{rpi} \leq V_s$ to $V_{wi} = V_s - V_{rpi}$, $i = 1, 2, ..., n$
- Discharge of rainwater from the tank to sewers:
  If $V_{rpi} + V_{di} \leq V_z$ to $V_{ki} = 0$, $i = 1, 2, ..., n$
  If $V_{rpi} + V_{di} > V_z$ to $V_{ki} = V_{rki} + V_{di} - V_z$, $i = 1, 2, ..., n$.

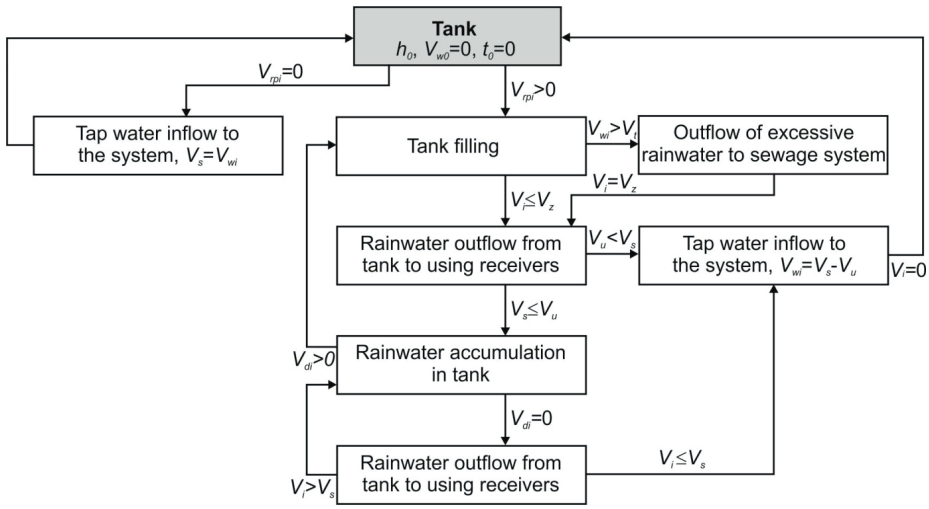

Fig. 3. Computing algorithm of Simulation Model of the economic use of rainwater utilization system (V_i – volume of rainwater retained in the tank at the end of day i, [m^3]; V_{di} – volume of rainwater inflowing on day i, [m^3]; V_{rki} – volume of retained rainwater in the tank after intake by installation on day i, [m^3]; V_{rpi} – volume of rainwater retained in the tank before intake by installation on day i, [m^3]; V_s – volume of water utilized by installation, [m^3]; V_u – volume of rainwater inflowing from retention tank to installation, [m^3]; V_{wi} – volume of mains water transported to installation on day i, [m^3]; V_z – rainwater tank capacity, [m^3])

Precipitation data

In the research carried out with the prepared simulation model of the rainwater utilization system in the university building, real precipitation data were used. The daily precipitation data originated from the meteorological station Rzeszow-Jasionka. For the simulation study, data from the period between 2003 and 2012 were used, for which annual totals are shown in Fig. 4. The average annual precipitation for the analyzed period was 695.35 mm and this does not diverge substantially from the multi-year average annual precipitation. Therefore, it may be assumed that the precipitation data used in the simulation model would provide reliable calculation results.

Figure 5 shows the daily precipitation for the year chosen from the analyzed period with an indicated spring-summer period where the highest rainfall is visible. The remaining days of the year constitute the autumn-winter period with prevailing snowfall.

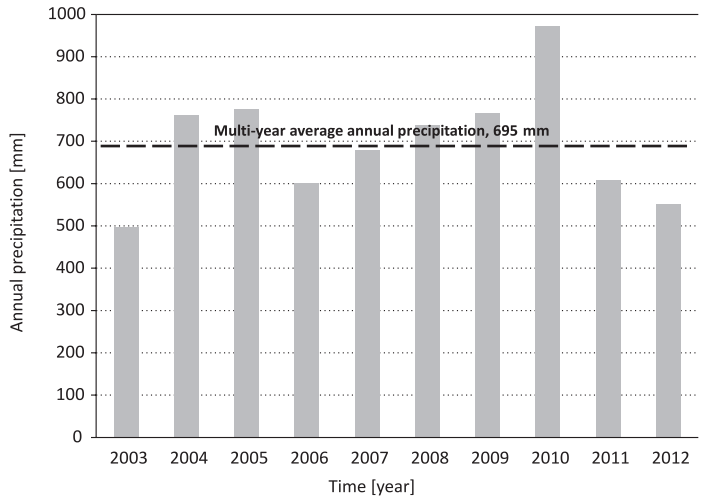

Fig. 4. Annual precipitation between the year 2003 and 2012

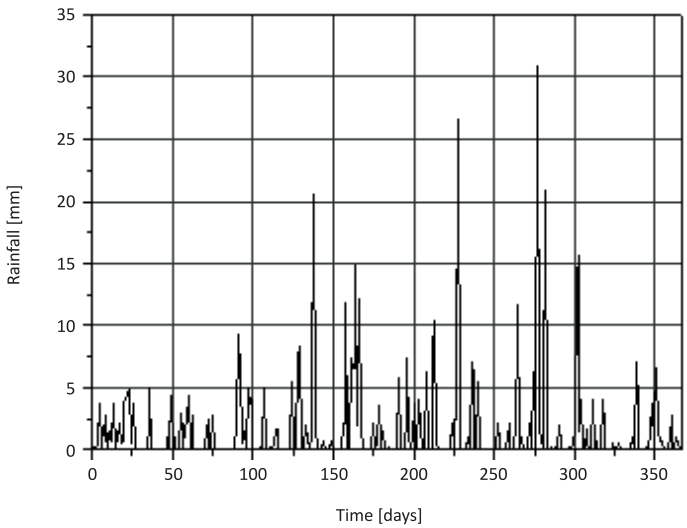

Fig. 5. Daily precipitation in the year 2012

Model input data

The analysis of the performance of the economic use of rainwater utilization system for the "Ikar" dormitory was carried out with a simulation model based on the following input data:

– Canteen roof surface F_S = 1714 m^2;
– Dormitory roof surface F_D = 731.9 m^2;
– Total drained surface F = 2445.9 m^2;

– Number of inhabitants (students) P = 600 persons;
– Average unit water requirement for toilet flushing q_s = 0.035 m^3/P/day;
– Daily water requirement for toilet flushing $V_s = q_s \cdot M$ = 21 m^3/day;
– Runoff index of a drained surface ψ = 0.9;
– Number of days of water retention in a tank during a period of drought t = 7 days.

The unit water requirement for toilet flushing q_s was determined on the basis of the statistical data concerning the structure of water consumption in Poland [38].

Based on the data characterizing the analyzed building and the recommendations of the manufacturers of rainwater tanks, the required capacity of the tank was calculated to be 90 m^3. In the study, this capacity was accepted as a reference value. Nevertheless, in order to conduct a deeper study of the *RWHS* performance in the analyzed object and determine the financial effectiveness of the investment project, two smaller capacities of the tank were also considered, namely, 60 and 30 m^3.

Results and discussion

On the basis of the prepared simulation model and possessed daily precipitation data the analysis of the performance of the economic use of rainwater utilization system for the chosen university facility. Figure 6 shows a graph illustrating filling trends in a period of 10 years in the tank. Figure 7 shows the collection process for rainwater from this tank on specific days of the chosen year.

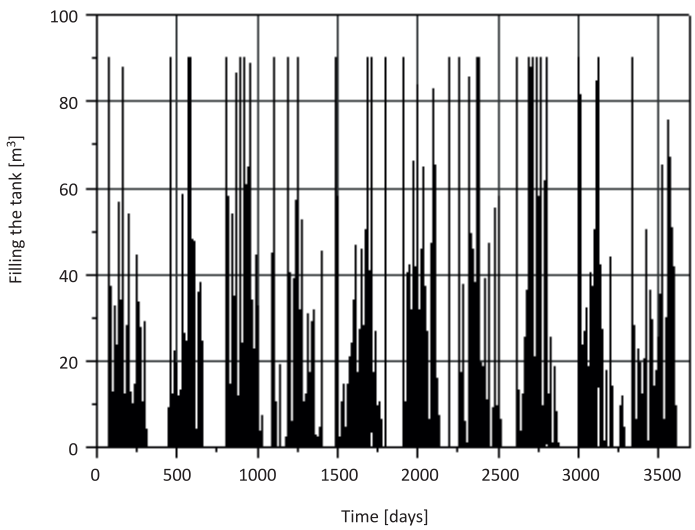

Fig. 6. Filling trends in the storage tank of rainwater for the "Ikar" dormitory with a tank capacity of 90 m^3 and a period between the 2003 and 2012

The collection of 21 m^3/day of water means that the total daily water requirement for toilet flushing in the "Ikar" dormitory is satisfied with the rainwater stored in tank.

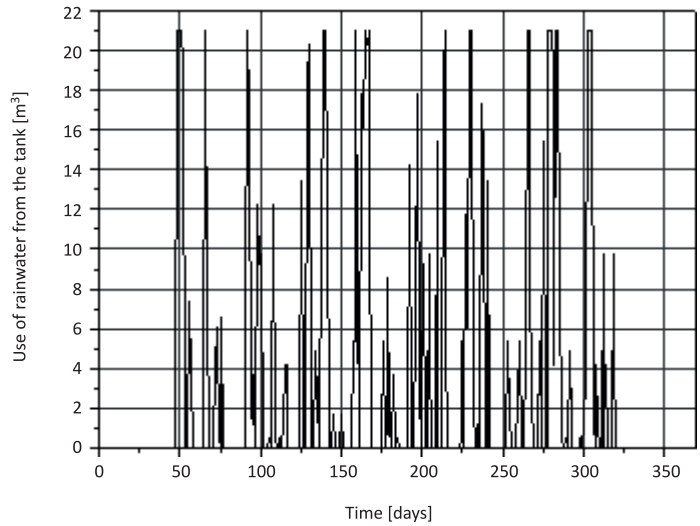

Fig. 7. Use of rainwater from the storage tank for toilet flushing in the "Ikar" dormitory with a tank capacity of 90 m^3 in 2012

A lower collection of water from this tank means that the rainwater quantity is insufficient and it is necessary to provide tap water from a water supply system. This process for a sanitary system in the "Ikar" building for an example year is shown in Fig. 8.

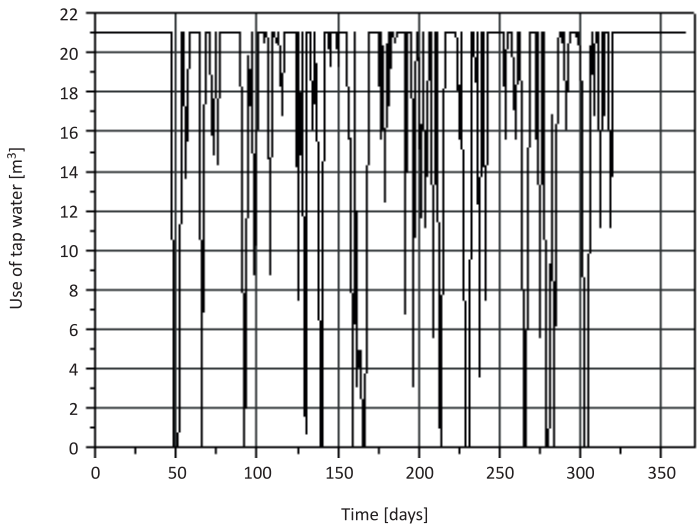

Fig. 8. Use of tap water for toilet flushing for the "Ikar" dormitory with the tank capacity of 90 m^3 in the year 2012

Despite of considerable capacity of the tank, which enables the rainwater downflows from a roof to be effectively retained in it, within the analyzed period some incidents

were observed when the excess of rainwater was discharged to a sewage system. Such situations happened mainly in summer periods in which considerably higher precipitation occurred and in the early spring periods when the snow cumulated on the roof melts. The discharging process of the excess of rainwater out of the system is shown in Fig. 9.

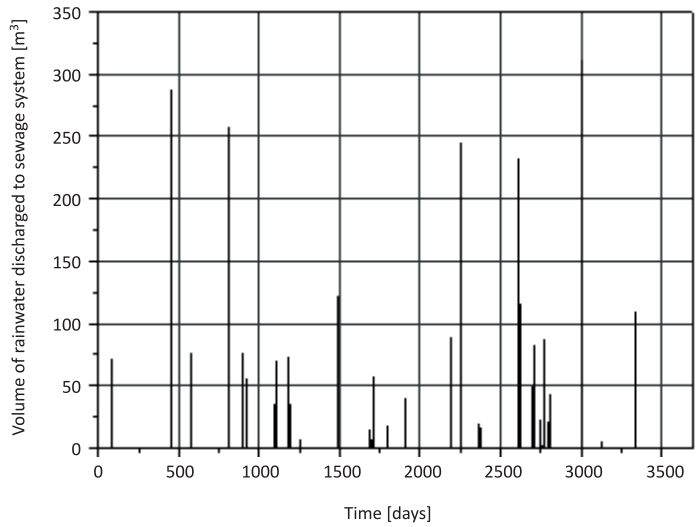

Fig. 9. Volume of an excess of rainwater discharged to a sewage system for the "Ikar" dormitory with the tank capacity of 90 m^3 and a period between the year 2003 and 2012

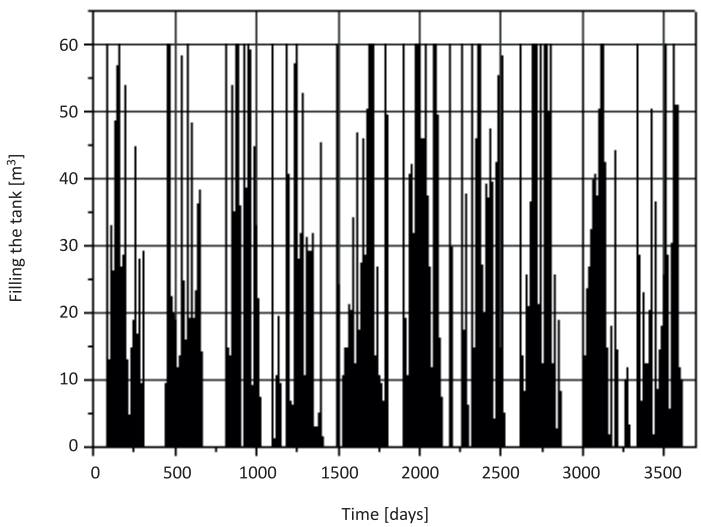

Fig. 10. Filling trends in the storage tank of rainwater for the "Ikar" dormitory with a tank capacity of 60 m^3 and a period between the 2003 and 2012

In the study it was also analyzed the influence of a retention tank size on efficiency of the economic use of rainwater utilization system for the "Ikar" dormitory. For the purposes of the analysis, tank capacities of 30 and 60 m^3 was assumed. Figure 10 shows the filling trends in tank with a capacity of 60 m^3, while Fig. 11 shows trends in the tank with a capacity of 30 m^3. Along with the decrease in the tank capacity, the volume of

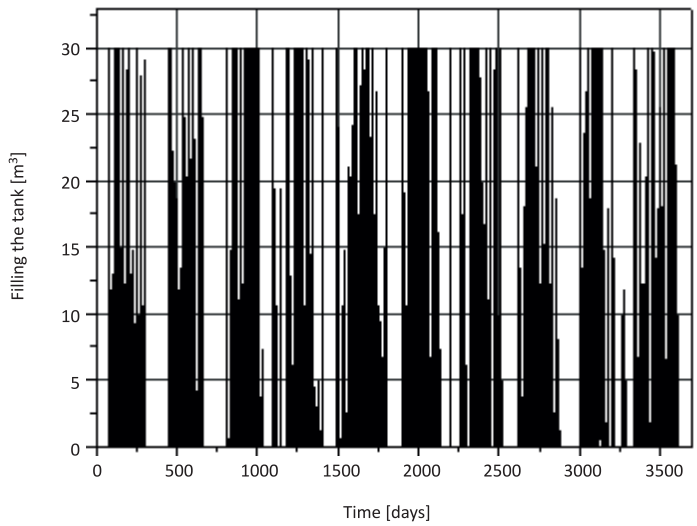

Fig. 11. Filling trends in the storage tank of rainwater for the "Ikar" dormitory with a tank capacity of 30 m^3 and a period between the 2003 and 2012

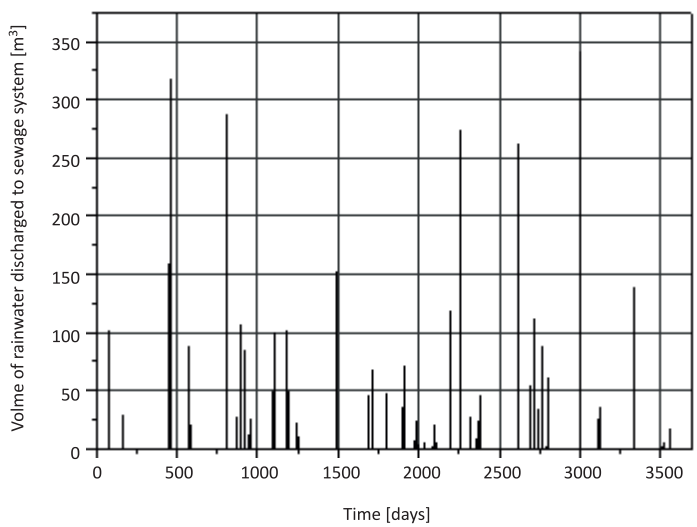

Fig. 12. Volume of an excess of rainwater discharged to a sewage system for the "Ikar" dormitory with the tank capacity of 60 m^3 and a period between the year 2003 and 2012

the rainwater excess discharged to the sewage system increases what is shown in Fig. 12 and 13.

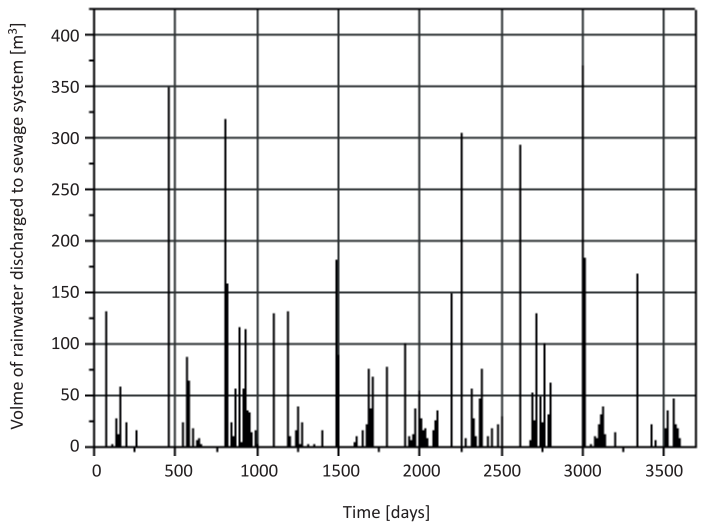

Fig. 13. Volume of an excess of rainwater discharged to sewage system for the "Ikar" dormitory with the tank capacity of 30 m^3 and a period between the year 2003 and 2012

Analyzing a period of 10 years it was found out that the rainwater downflows from a roof coating cannot fully substitute the tap water needed to satisfy the daily demand for toilet flushing. The high proportion of tap water in the water requirement for toilet flushing resulted from the undersized roof surface and the irregular occurrence of precipitation within the year. On the basis of these findings, for each analyzed variant of retention tank capacity, the percentage share of rainwater in the total water requirement for toilet flushing in the "Ikar" dormitory was calculated. It was discovered that the most effective utilization of rainwater occurs with a storage tank of 90 m^3 capacity. Figure 14 shows the results of the research for the 10-year period and the three variants of tank capacity.

Depending on the retention tank capacity, an average saving on lower quality water was 11 to 22%. This low system efficiency in the case of a multi-storey building such as the "Ikar" building is a consequence of the undersized roof surface from which the rainwater is collected and, also of the considerable water requirement from the large number of inhabitants.

In the discussed variants of retention tanks, the possible accumulation of rainwater downflows from the roof is high, and increases along with an increase in tank capacity. The 90 m^3 tank can store an average 85% of rainwater downflows from the roof, while the retention of the smallest tank is 66%. A smaller proportion of accumulation of the rainwater downflows from the roof to tank was either the result of the irregular occurrence of precipitation within the year or substantial amount of heavy rain during which the excess water was discharged from the tank to the sewage system. The

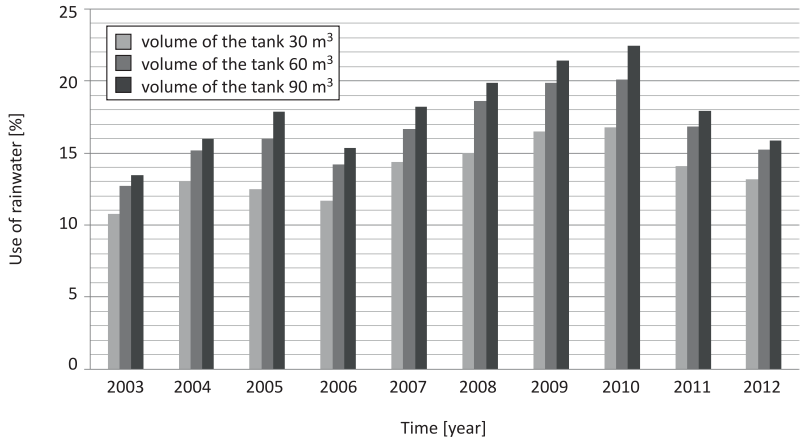

Fig. 14. Percentage share of rainwater in the total water requirement for toilet flushing for the "Ikar" dormitory tank variant capacities between 2003 and 2012

contribution of rainwater accumulated in the tank in relation to the total volume of rainwater brought into the tank from the building's roof is shown in Fig. 15.

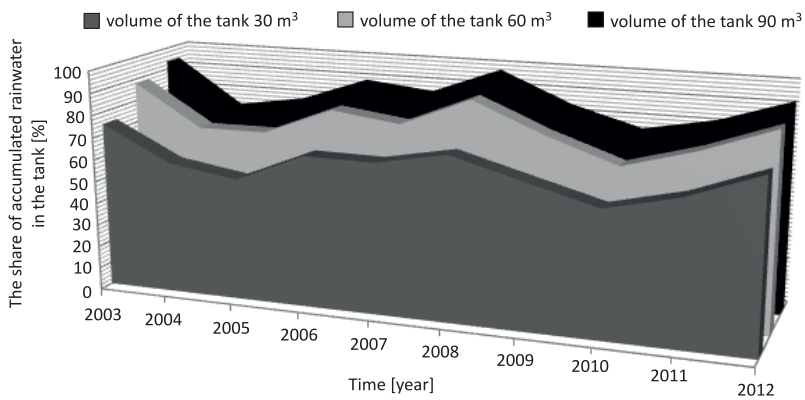

Fig. 15. Contribution of rainwater accumulated in the tank in relation to the total volume of rainwater brought into the tank from the roof

Economic effects of using rainwater harvesting system in the "Ikar" dormitory"

First and foremost, the economic effect of the use of a rainwater utilization system depends on the possible savings on tap water, and capital expenditures and operating costs borne during the system's operation.

The results of the simulation study obtained for different variants of tank capacity enabled us to assess the financial effectiveness of an investment in the possible

utilization of rainwater for toilet flushing in the analyzed university facility, and define an optimum variant for the capital project. For this purpose, for the analyzed variant two financial ratios have been determined: the Net Present Value (*NPV*) and the Discounted Payback Period (*DPP*).

The Net Present Value (*NPV*) is the sum of all net profits generated by the investment during the entire operating period of a specific facility, which are discounted before totalization [39]. If the *NPV* value is greater than zero it means that the revenue from the undertaking exceeds the capital expenditures in value and a given investment project is therefore profitable. On the other hand, if the *NPV* value is less than zero it means that a given investment project is unprofitable. The net present value for each study variants *k* of the rainwater system utilized for toilet flushing was determined from mathematical relation (1).

$$NPV_k = \sum_{t=0}^{n} \frac{CF_{kt}}{(1+r)^t} \tag{1}$$

where: CF_{kt} – cash flows in the year *t*, calculated from Eq. (2), [€];
r – the discount rate, r = 5%;
n – number of years of the operation of the system, n = 30 years.

The discount rate for the Net Present Value was assumed to be 5%, as it was used in calculations by Morales-Pinzon et al [40], Roebuck et al [33] and Liaw and Tsai [41].

The cash flow value CF_{kt} for particular years was defined as the sum of investments INV_{kt} borne in a given year and savings O_{kt} resulting from the economic use of the precipitation water utilization system (2).

$$CF_{kt} = -INV_{kt} + O_{kt} \tag{2}$$

where: INV_{kt} – investment in the year *t*, [€];
O_{kt} – savings in the year *t*, calculated from Eq. (3), [€].

Calculations included the savings resulted from the reduced collection of tap water and a reduction in rainwater volumes discharged to the sewage system. The savings in consecutive years of system operation were determined using mathematical relation (3).

$$O_{kt} = (W_{0t} - W_{kt}) \cdot C_{Wt} + (R_{0t} - R_{kt}) \cdot C_{Rt} \tag{3}$$

where: O_{kt} – savings resulted from the economic use of a rainwater utilization system in particular years, [€];
W_{0t} – water utilization for toilet flushing in variant 0 without the use of a rainwater water utilization system, [m^3];
W_{kt} – water utilization for toilet flushing in variant *k* with the use of a rainwater water utilization system, [m^3];
C_{Wt} – tap water purchase price in consecutive years, [€/m^3];
R_{0t} – rainwater volume discharged from the roof to the sewage system in variant 0 without the use of a rainwater utilization system, [m^3];

R_{kt} – rainwater volume discharged from the roof to the sewage system in variant k with the use of a rainwater utilization system, [m^3];
C_{Rt} – price for rainwater discharge to the sewage system in consecutive years, [€/m^3].

For calculations of financial savings O_{kt} the following price values were assumed: C_{Wt} = 1 €/m^3, C_{Rt} = 0.7 €/m^3. In that research, the annual increase in prices was also taken into account for the entire period of RWHS operation. On the basis of the archival data concerning the water rates and wastewater discharging fees in Rzeszow, the trend curve concluded that the annual water rate-raising was approximately 8% while the rate-raising was 4% for the rainwater discharged to the sewage system.

On the basis of these data and the results obtained from the simulation model tests, the cash flows were calculated for a period of 30 years of system operation and each assumed retention tank capacity variant. The results of the calculations are shown in Fig. 16.

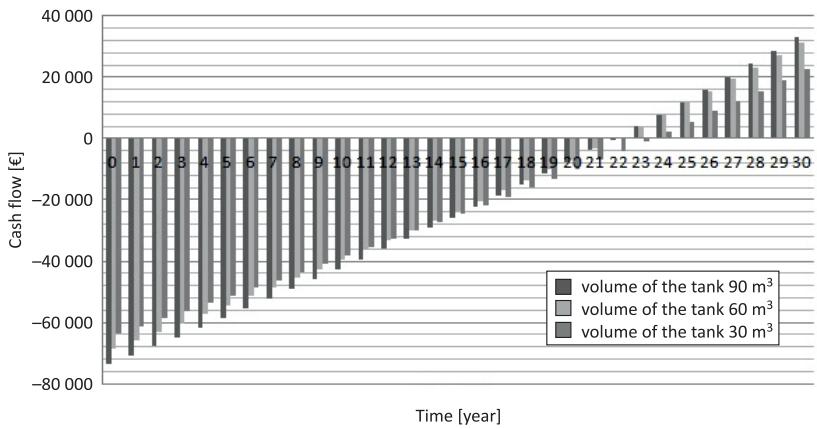

Fig. 16. Cash flow values for the analyzed economic use of rainwater utilization system in the "Ikar" dormitory over a period of 30 years

The annual cash flow values obtained enabled us to determine the *NPV* of investment undertaking for the analyzed variants. Nevertheless, in order to check the influence of tap water buying costs on the *NPV* of the supply of a sanitary system with rainwater two scenarios were analyzed in which an annual increase in water price by 6 and 10% was assumed. The capital expenditures borne in the zero-year included expenditures resulting from the purchase costs of the tank, installation materials, necessary inbuilt plumbing fittings and construction costs of the entire system. Depending on the variant of retention tank capacity, the value of these expenditures for the tank capacity of 30 m^3, 60 m^3 and 90 m^3 was 63 734, 68 784 and 73 833 Euro respectively. Moreover, the annual operating expenses of the rainwater utilization system in the analyzed building include the cost of water pumping from the tank to the sanitary system. Figure 17 shows the functional dependency of the *NPV* on the forecast increase in tap water purchase prices.

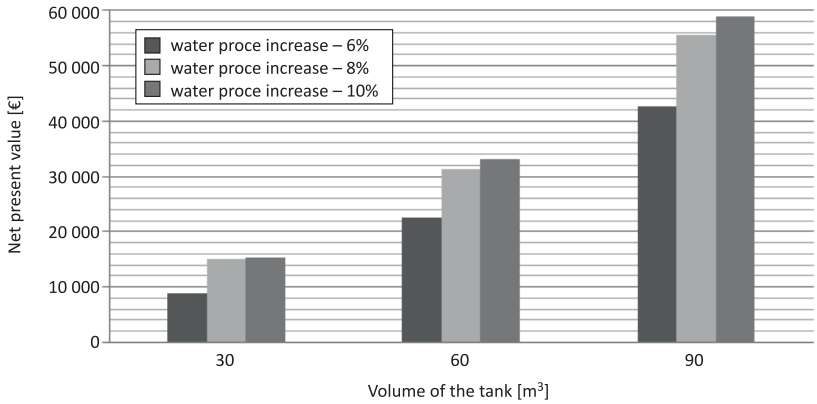

Fig. 17. Net Present Values for the economic use of a rainwater utilization system in the "Ikar" dormitory relative to the tank capacity and assumed increase in tap water purchase prices over a period of 30 years

On the basis of the findings obtained, it can be noted that for the assumed scenarios of increase in tap water purchase prices the *NPV* for each analyzed variant is greater than zero. This means that for the weather data used from a period of 10 years and independently of the retention tank capacity every variant of the investment is profitable. The increased tap water purchase prices resulted in an increase in *NPV*, which became more apparent when the tank capacity was enlarged. The assumed 10% price increase is greater than this one calculated on the basis of historical data, but taking into consideration current forecasts for increases in tap water purchase prices and Poland's shrinking water resources, such a scenario is highly probable.

The next financial ratio to be analyzed was the Discounted Payback Period (*DPP*), calculated using mathematical relation (4). This financial ratio determines the number of years after which the discounted incomes from a realized undertaking compensate for the capital expenditures [42].

$$DPP_k = Y_k + \frac{|NPW_{kY}|}{CF_{(kY+1)}} \tag{4}$$

where: DPP_k – Discounted Payback Period determined for a variant k, [yr.];
Y_k – number of full years before a total payback of expenditures determined for a variant k, [year];
$CFk_{(Y+1)}$ – discounted cash flow in a year $(Y + 1)$, determined for a variant k, [€];
NPV_{kY} – unrecovered expenditures determined at the beginning of the year $(Y + 1)$, determined for a variant k, [€].

The Discounted Payback Period was calculated for three analyzed variants of rainwater retention tank capacity in the economic use of a precipitation water utilization system in the "Ikar" dormitory. The findings are presented in Table 1.

Table 1

Discounted Payback Period for analyzed variants of the rainwater utilization system

Tank capacity [m^3]	Discounted Payback Period [year]
30	23.3
60	21.9
90	22.0

On the basis of the findings obtained, it can be seen that in no analyzed variant of rainwater retention tank capacity did the payback period exceed the one which was assumed for the system's operational life in the building. In the most profitable of the analyzed variants, *ie*, the tank of 60 m^3 capacity, the *DPP* is 21.9 year. Nonetheless, because of very similar values of that ratio for the analyzed variants of the investment projects, it cannot be considered as a critical parameter in the decision-making process. Therefore in the analyzed building, the determined *NPVs* should be taken into consideration first of all.

In order to assess the investment risk connected with the economic implementation of rainwater utilization systems in the analyzed dormitory, the investment sensitivity analysis was conducted. For that purpose, the investment sensitivity indexes *sc* were determined which illustrated to what extent the change in value of independent variables by 1% could influence the obtained *NPV* value. In that method, it is assumed that only a single independent variable is changed at the given moment while the other variables remain at the same basis level. Furthermore, within that analysis the relative safety margins *sm* have also been calculated which define the allowable deviation of the given variable from the basis value at which the investment project is still cost-effective [43]. The calculation was made using the dependences.

$$sc = \frac{\dfrac{NPV_i - NPV_b}{NPV_b}}{\dfrac{Z_i - Z_b}{Z_b}} \tag{5}$$

where: sc – NPV sensitivity index against the change in value of variable Z by 1%;
Z_i – i-value of the variable;
NPV_i – NPV value at the i-value of variable Zi;
Z_b – basis value of variable Z;
NPV_b – NPV value for the variable Z_b.

$$sm = \frac{Z_g - Z_b}{Z_b} \tag{6}$$

where: sm – investment safety margin;
Z_g – limit value of the analyzed variable.

The research also analyzed the influence of increase in investment expenses by 1% on *NPV* as well as the reduction in possible savings by 1% which resulted from the fact that an increase in water rates and wastewater discharge fees for rainwater discharged to the sewage system were changed to a lesser extent than it was assumed.

The values of sensitivity indexes *sc* and relative safety margins were determined for all cases analyzed in this paper, because for all *NPVs* get positive values and this indicates that the analyzed project is cost-effective. The obtained results of calculations are tabulated in Table 2.

Table 2

The summary of calculated values of the sensitivity index *sc* and the relative safety margin *sm*

The analyzed independent variable	Sensitivity index *sc*	Relative safety margin *sm* [%]
The volume of the tank: 30 m^3		
Investment	–4.25	23
Tap water price	3.37	–29
Price for rainwater discharge to the sewage system	2.37	–42
Tap water price + Price for rainwater discharge to the sewage system	5.74	–17
The volume of the tank: 60 m^3		
Investment	–2.19	45
Tap water price	1.93	–52
Price for rainwater discharge to the sewage system	1.25	–79
Tap water price + Price for rainwater discharge to the sewage system	3.18	–31
The volume of the tank: 90 m^3		
Investment	–1.33	75
Tap water price	1.17	–84
Price for rainwater discharge to the sewage system	0.74	–133
Tap water price + Price for rainwater discharge to the sewage system	1.91	–51

The obtained values of sensitivity indexes and safety margins demonstrated that the investment project including the use of the *RWHS* in the analyzed dormitory is most sensitive to the changes in savings caused to a lesser extent by an increase in water-rates and wastewater discharge fees for rainwater discharged to the sewage system. Also it was observed that along with increasing tank capacity, the investment sensitivity index decreased $|sc|$, and for the capacity of 90 m^3 it reached the value of 1.91, at the relative safety margin $|sm|$ of –51%. It means that for that tank capacity the capital expenditures could be increased by 75% and savings reduced by 51% and, even so, the investment will still be profitable. Definitely, the project with the tank capacity of 30 m^3 is less sensitive to the capital expenses and the water purchasing prices as well as the wastewater discharging fees. In this case, the relatively high values of the sensitivity

indexes |*sc*| testify to the great influence of the analyzed variables on the cost-efficiency of the analyzed investment project. Also, it is evidenced by the determined relative safety margins |*sm*|. For that investment variant, the capital expenses could be increased merely by 23% and the savings reduced by 17%. Otherwise, the undertaking becomes unprofitable.

The conducted sensitivity analysis demonstrated that together with an increase in the capacity of the rainwater tank in the analyzed *RWHS*, the investment sensitivity decreases in either case, namely, an increase in capital expenses born in the year "zero" ("0") and the savings gained during the system operational life-cycle in the building. It was also observed that the directions of changes in the capital expenses and cost-effectiveness of the analyzed undertaking are opposed to each other. It is evidenced by the obtained values of the investment sensitivity indexes ($sc < 0$) as well as the relative safety margins ($sm > 0$). It means that the financial effectiveness of the analyzed investment project increases along with the decrease in capital expenses. However, in the case of changes in the purchasing prices of the tap water and the wastewater discharging fees for the rainwater discharged to the sewer, the direction of such changes corresponds to the direction of changes of the investment profitability level. The increase in those two prices causes an increase in savings resulting from the *RWHS* implementation in the analyzed building, and it consequently led to an increase in the updated *NPV* values.

Conclusion

The accumulation and utilization of rainwater provides many advantages for sustainable urban development and is a key point in strategies used to reduce water shortages in urban conditions.

The elaborated simulation model is versatile and can be used for research on the rainwater harvesting system performance in different buildings as well as for different climatic conditions and the results obtained due to the use of it enable the financial effectiveness to be determined for this type of undertakings.

This paper presents the result of the case study where it is planned to implement the *RWHS*. Therefore, the findings may provide valuable guidelines for the investor in making decisions on the implementation of the *RWHS* in the analyzed dormitory building.

This study on the possible use of a rainwater harvesting system (*RWHS*) in a dormitory enables the following set of conclusions to be formulated.

1. The use of rainwater harvesting system enables tap water consumption for toilet flushing in the analyzed facility to be reduced by 11 to 22% depending on the capacity of the retention tank used.

2. The efficiency of rainwater harvesting system is limited by the roof size from which the rainwater is collected. An increase in this surface area will provide a substantial increase in tap water savings and improve the cost-effectiveness of the investment. Because of this, it would be profitable to deliver rainwater from the roofs of

neighboring buildings to the retention tank. Furthermore, a decrease in the water consumption for toilet flushing will increase the savings.

3. The use of an RWHS in the facility studied is financially profitable. In no analyzed variant of rainwater retention tank capacity did the discounted payback period *DPP* exceed the obtainable "life cycle" of the system in the building.

4. Together with an increase in a tank capacity, the updated investment *NPV* increased as well and it reached its highest value for the tank capacity of 90 m^3.

5. The conducted sensitivity analysis demonstrated that together with increasing tank capacities the *RWHS* implementation undertaking for the analyzed dormitory is less sensitive to both the changes in capital expenses and obtainable financial savings.

6. The use of the *RWHS* with the tank of 90 m^3 capacity enables not only the best financial parameters to be gained, but also the rainwater volumes discharged to the sewage system to be reduced what could favorably influence the drainage system performance as well as the protection of receiving bodies of water, which are most commonly surface flowing waters.

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MOŻLIWOŚCI WYKORZYSTANIA WODY DESZCZOWEJ W DOMU STUDENCKIM: OSZCZĘDNOŚĆ WODY PITNEJ I KORZYŚCI FINANSOWE

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Abstrakt: W pracy przedstawiono wyniki badań określające efektywność finansową systemu wykorzystania wody deszczowej (*RWHS*) do spłukiwania toalet. Jako przedmiot badań wybrano budynek mieszkalny (akademik) zlokalizowany w Polsce. Analizę funkcjonowania systemu *RWHS* przeprowadzono na sformułowanym modelu symulacyjnym. W badaniach przeanalizowano również wpływ wielkości zbiornika retencyjnego na efektywność finansową zastosowania systemu gospodarczego wykorzystania wody deszczowej w rozpatrywanym domu studenckim. W analizie finansowej zostały określone dwa wskaźniki finansowe: wartość bieżąca netto (*NPV*) oraz zdyskontowany okres zwrotu (*DPP*). W celu oceny ryzyka inwestycyjnego związanego z zastosowaniem systemu gospodarczego wykorzystania wody deszczowej w badanym akademiku wykonano analizę wrażliwości inwestycji. W tym celu wyznaczono współczynniki wrażliwości inwestycji *sc*, które obrazują, jak duży wpływ na otrzymaną wartość *NPV* wywiera zmiana wartości poszczególnych zmiennych niezależnych o 1%. Przeprowadzona analiza wykazała, że zastosowanie układu RWHS w analizowanym budynku jest opłacalne i może zmniejszyć zapotrzebowanie na wodę do spłukiwania toalet od 11 do 22%, w zależności od pojemności zbiornika retencyjnego.

Słowa kluczowe: systemy wykorzystania wody deszczowej, zarządzanie wodą deszczową, oszczędność wody pitnej, analiza finansowa

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Beata BIEŃ[1]

THE QUALITY OF SLUDGE LIQUIDS PRODUCED IN THE PROCESS OF MECHANICAL DEWATERING OF DIGESTED SLUDGE

JAKOŚĆ CIECZY OSADOWYCH POWSTAJĄCYCH W PROCESIE MECHANICZNEGO ODWADNIANIA OSADÓW PRZEFERMENTOWANYCH

Abstract: The quality of sludge liquids produced in the processes of mechanical dewatering of sludge depends on the stabilization technology and the kind of device, its proper operation, and an appropriate choice of conditioning chemicals. The article presents the impact of selected conditioning chemicals and methods, such as: PIX 113, PIX 123, Zetag 8160 polyelectrolyte, ultrasonic field, and their combined effect on the properties of sludge liquids. crude sludge liquids were characterized by high concentrations of ammonium nitrogen (931–1,508.9 mg $N\text{-}NH_4^+/dm^3$), phosphates (24.3–89.4 mg PO_4^{3-}/dm^3) and organic compounds referred to as COD (784–1,856 mg O_2/dm^3). It was found that the combined effect of inorganic coagulant PIX 123 and polyelectrolyte allowed the reduction of suspended solids and COD in sludge liquids. In the case of suspension, the highest reduction (53.8%) was obtained when using PIX 123. With regard to the changes of COD, similar effects were obtained for PIX 123 (43%) and the combined method (41.6%). The use of the PIX 113 coagulant and Zetag 8160 polyelectrolyte increased the ratio of total suspended solids in the sludge liquids in relation to crude sludge liquids. The PIX 113 coagulant led to reducing the values of COD (90%), ammonium nitrogen (14.9%) and phosphates (93.8%) with relation to crude sludge liquids. Zetag 8160 alone proved to be the least effective.

Keywords: sludge liquids, coagulants, polyelectrolytes, ultrasonic field, mechanical dewatering

Introduction

Improving the efficiency of sewage treatment by means of using integrated systems to remove nitrogen and phosphorus compounds from sewage results in greater sludge volume and changes in the qualitative parameters of sludge, caused *ie*, by substantial accumulation of phosphorus in bacteria cells. During sewage treatment in anaerobic conditions (methane fermentation), even 60% phosphorus removed from the sewage may be discharged again during the hydrolysis of polyphosphates to sludge liquid [1, 2]. It

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was also found that 70% of total nitrogen introduced together with crude sludge to the digestion chamber got to sludge liquid in the form of ammonium nitrogen [3]. Besides, sludge liquid has high contents of organic compounds, total, non-settling and colloidal suspensions, dissolved gases (methane, ammonia, CO_2, H_2S), heavy metals, fats, and ammonia. In liquid digestate there are also high concentrations of volatile fatty acids (VFAs), carbonates, and potassium and magnesium cations [4, 5]. The intensification of sewage sludge processing, motivated by the pursuit of easy management of the end product, results in increased influence of the sludge processing line on the operation of sewage treatment technological line [6]. Including all untreated reject water in the stream of crude sewage, which is still the standard method, has a definitely detrimental effect on the conditions of operation of biological reactors through reducing the ratio of the content of biologically decomposing organic compounds and the content of nutrients, especially nitrogen. The total nitrogen concentration in crude sewage, caused by mixing sewage with untreated sludge waters, in typical technological systems, increases approximately by 20% [7, 8]. The problem of sewage management return loads is more and more often the object of research [9–13]. The amount and quality of sludge liquids mainly depend on the adopted technological system of sewage treatment and sewage sludge processing (especially the way of stabilization and dewatering) as well as the performance of devices in the sewage process line [14, 15]. The proper choice of polyelectrolyte or filter fabric is often decisive, not only for thickening or dewatering of sludge but also for the quality of liquids discharged from the devices [16]. Taking into account the importance of sludge liquid quality, the article presents the influence of selected conditioning chemicals and methods, such as: PIX 113, PIX 123, Zetag 8160 polyelectrolyte, ultrasonic field, and their combined effect on the properties of sludge liquids.

Material and methods

Sewage sludge after the process of methane fermentation was used in the experiment. The experiment included two parts. Digested sludge samples used in each part were collected on two different days and marked digested sludge A and B. In the first part, non-sonicated and sonicated digested sludge A was studied. Sludge A was conditioned with PIX 123, Zetag 8160, and the method combining 1.0 mg/g d.m. (d.m. – dry matter) of PIX 123 and different doses of Zetag 8160: 0.5; 1.5; 2.5; 3.5 mg/g d.m. In the second part, non-sonicated and sonicated digested sludge B was studied. It was treated with PIX 113 and the method combining 4.5 mg/g d.m. of PIX 113 and different doses of Zetag 8160: 1.5; 2.5; 3.5 mg/g d.m. Samples of sludge liquid were obtained after the process of centrifugation of properly treated sewage sludge. The time of centrifugation was 5 min, and the speed, 5,000 rot/min. The characteristics of the coagulants are shown in Table 1.

In order to obtain a solution of Zetag 8160 polyelectrolyte, it was thoroughly mixed with water. After 120 minutes of mixing, the solution was mature and ready to use.

In the method combining the chemicals, PIX 123 (or PIX 113) coagulant was administered first, followed by Zetag 8160 polyelectrolyte. This way both reagents are used to the full and can influence each other.

Table 1

Characterization of chemicals used in the research

Coagulant	Coagulant properties
PIX 123	A dark brown solution of ferric sulfate, with total iron (Fe) content of 12.6 ± 0.3%, and iron ions Fe^{+2} content of max 0.7%.
PIX 113	A ferric coagulant, a dark brown water solution of ferric sulfate, with total iron (Fe) content of 11.4 ± 12.2%, and iron ions Fe^{+2} content of 0.4 ± 0.3%.
Zetag 8160	A synthetic polyacrylamide with a high molecular mass, provided as loose white powder. Zetag 8160 is a cation polyelectrolyte.

In order to obtain a solution of Zetag 8160 polyelectrolyte, it was thoroughly mixed with water. After 120 minutes of mixing, the solution was mature and ready to use.

In the method combining the chemicals, PIX 123 (or PIX 113) coagulant was administered first, followed by Zetag 8160 polyelectrolyte. This way both reagents are used to the full and can influence each other.

The sewage sludge was sonicated in static conditions, with a constant sample volume of 0.3 dm^3. An high power, microprocessor-based ultrasonic processor Sonics VC750 with automatic tuning, the frequency of 20 kHz and amplitude of 30.5 μm (corresponding to the 50% amplitude) was used to sonicate the samples. The variable of the sonication process was the disintegration time t = 60 s.

The following parameters were determined in the sludge liquid: pH with the potentiometric method (pH-meter CP401 from Elmetron), total suspended solids with the weighing method, COD with the short dichromate method (PN-ISO 6060:2006), ammonium nitrogen and phosphates PO_4^{-3} as well as total phosphorus (P_{og}) with the spectrophotometric method (Spectrophotometer JENWAY 6300). The following conditioners were used in the research: 10% solution of PIX 123 and PIX 113 coagulant, 0.1% solution of Zetag 8160 polyelectrolyte, ultrasonic field.

Results and discussion

Crude sludge liquids had very high concentrations of ammonium nitrogen (931–1,509 mg $N\text{-}NH_4^+/dm^3$), phosphates (24.3–89.4 mg PO_4^{3-}/dm^3) and organic compounds referred to as COD (784–1,856 mg O_2/dm^3). The characterization of the sludge liquids is shown in Table 2.

In samples of sludge liquid (Table 3) obtained from non-sonicated and sonicated sludge A treated with PIX 123 the pH value dropped. The pH value decreased with the increasing dose of the coagulant. For 3.5 mg/g d.m. it was 6.04 (reduced by 12.7%). In the liquid separated from non-sonicated and sonicated sludge A treated with Zetag 8160 and liquid treated with 1.0 mg/g d.m. of PIX 123 and different doses of Zetag 8160, the pH value grew with the growing dose of the chemicals used (Table 3). In the case of all the analyzed methods of conditioning, the amount of suspended solids in sludge liquids decreased as the dose of reagents increased. The greatest reduction was 53.8% (for 3.5 mg/g d.m. of PIX 123).

Table 2

Characteristics of sludge liquids

Determination	Unit	Crude liquids separated from digested sludge	
		A	B
pH	—	6.92	6.76
Suspension	mg/dm^3	1,300	280
COD	mgO_2/dm^3	1,856	784
Ammonium nitrogen	$mgN\text{-}NH_4^+/dm^3$	1,509	931.5
Phosphates	$mgPO_4^{-3}/dm^3$	89.4	24.3
Phosphorus	$mgP\text{-}PO_4^{-3}/dm^3$	29.2	7.94

In samples of sludge liquid (Table 3) obtained from non-sonicated and sonicated sludge A treated with PIX 123 the pH value dropped. The pH value decreased with the increasing dose of the coagulant. For 3.5 mg/g d.m. it was 6.04 (reduced by 12.7%). In the liquid separated from non-sonicated and sonicated sludge A treated with Zetag 8160 and liquid treated with 1.0 mg/g d.m. of PIX 123 and different doses of Zetag 8160, the pH value grew with the growing dose of the chemicals used (Table 3). In the case of all the analyzed methods of conditioning, the amount of suspended solids in sludge liquids decreased as the dose of reagents increased. The greatest reduction was 53.8% (for 3.5 mg/g d.m. of PIX 123).

Table 3

Changes of selected parameters of sludge liquids from sludge A

Parameters of sludge liquids	Dose [mg/g d.m.]	pH [-]	COD [mg O_2/dm^3]	Suspension [mg/dm^3]
Sludge liquids separated from non-sonicated, digested sludge treated with different coagulants				
Crude sludge liquids	—	6.92	1,856	1,300
PIX 123	0.5	6.86	1,522	1,140
	1.5	6.59	1,465	850
	2.5	6.20	1,171	720
	3.5	6.04	1,057	600
Zetag 8160	0.5	7.21	1,729	1,220
	1.5	7.24	1,653	1,080
	2.5	7.34	1,622	930
	3.5	7.38	1,503	880
PIX 123 (1.0) + Zetag 8160*	0.5	6.97	1,240	1,260
	1.5	7.00	1,206	1,110
	2.5	7.23	1,156	1,020
	3.5	7.36	1,083	920

Table 3 contd.

Parameters of sludge liquids	Dose [mg/g d.m.]	pH [-]	COD [mg O_2/dm^3]	Suspension [mg/dm^3]
Sludge liquids separated from sonicated, digested sludge treated with different coagulants – the sonication time was 60 s, and the amplitude 30.5 μm				
Crude sludge liquids PIX 123	—	7.49	2,894	1,620
	0.5	7.30	2,122	1,250
	1.5	6.89	1,578	960
	2.5	6.61	1,135	820
	3.5	6.47	674	710
Zetag 8160	0.5	7.57	2,689	1,480
	1.5	7.67	2,558	1,190
	2.5	7.83	2,479	1,070
	3.5	7.87	2,128	930
PIX 123 (1.0) + Zetag 8160*	0.5	7.14	1,488	1,490
	1.5	7.22	1,422	1,220
	2.5	7.28	1,406	1,140
	3.5	7.32	1,386	1,010

* Sludge liquid obtained from sewage non-sonicated or sonicated sludge A, first treated with 1.0 mg/g d.m. of PIX 123 and then with different doses of Zetag 8160: 0.5; 1.5; 2.5; 3.5 mg/g d.m.

The amount of organic compounds (COD) in sludge liquids decreased during the process of sewage sludge conditioning. The efficiency of their removal grew with the growing dose in the case of each coagulant and the method combining PIX 123 and Zetag 8160 (Fig. 1). The best effect of organic compounds removal was observed for the liquid separated from sonicated sludge treated with PIX 123: between 26.7% and 76.7%. In the other methods the reduction in the amount of organic compounds was between 6.8% and 26.5% (for Zetag 8160) and between 33.2% and 52.1% (for the method combining PIX 123 and Zetag 8160).

In samples of sludge liquid (Table 4) obtained from non-sonicated sludge B treated with PIX 113 the pH value dropped. The pH value decreased with the increasing dose of the coagulant. For 5.5 mg/g d.m. of PIX 113 it was 5.57 (reduced by 17.6%). In the liquid samples treated together with 4.5 mg/g d.m. of PIX 123 and different doses of Zetag 8160, pH dropped to 5.70 (15.67%). The addition of the PIX 113 coagulant and Zetag 8160 polyelectrolyte increased the ratio of total suspended solids in relation to crude sludge liquids, and then the amount of suspended solids decreased as the doses of the reagents increased.

The content of phosphates and nitrogen decreased in all samples (Fig. 2). The lowest values of phosphates and ammonium nitrogen were observed for samples treated with PIX 113 (93.8% for phosphates and 14.9% for ammonium nitrogen, respectively). When

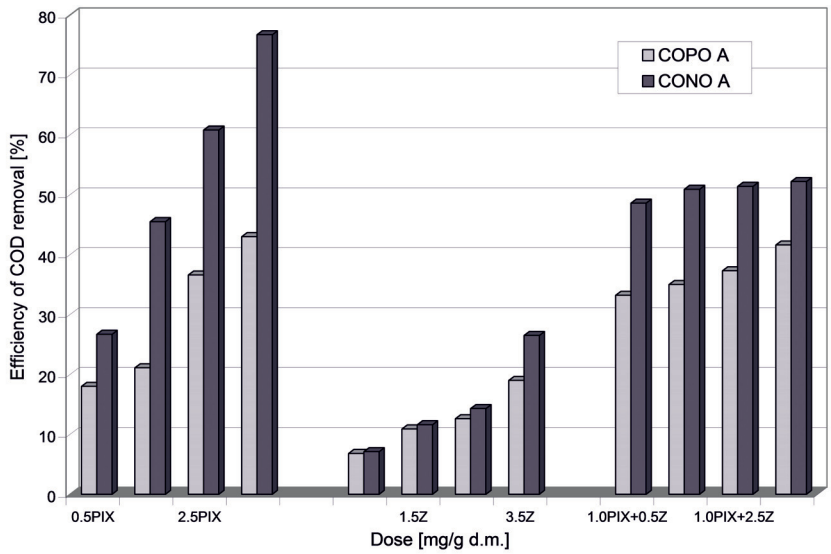

Fig. 1. Efficiency of COD removal in relation to dose and type of coagulant (COPO A – sludge liquid from digested sludge A, CONO A – sludge liquid from digested and sonicated sludge A)

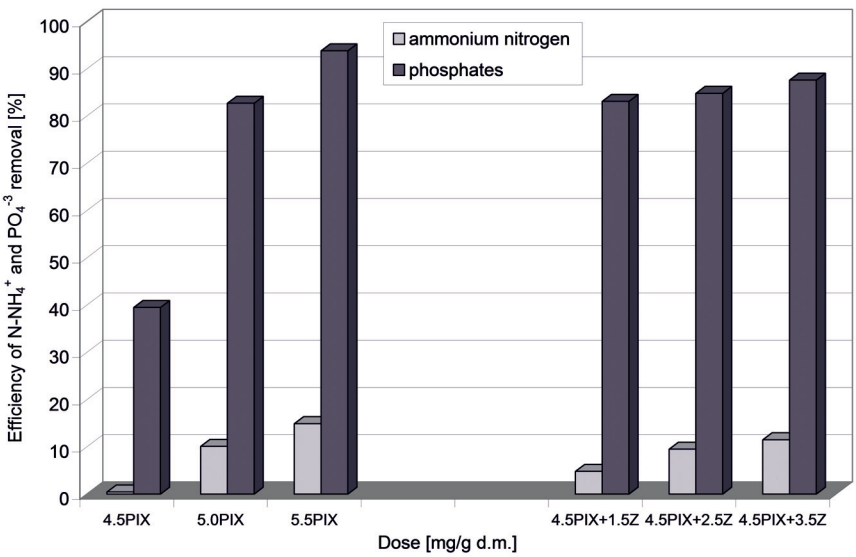

Fig. 2. Efficiency of ammonium nitrogen and phosphates removal depending on the dose and type of coagulant

using PIX 113, the phosphates content in the liquid dropped. This coagulant bound and retained the compounds in the sludge proportionally to the administered dose.

Table 4

Changes of selected parameters of sludge liquid from sludge B

Parameters of sludge liquids	Dose [mg/g d.m.]	pH [-]	Phosphates [mg PO_4^{-3}/dm^3]	Phosphorus [mg $P\text{-}PO_4^{-3}/dm^3$]	Ammonium nitrogen [mg $N\text{-}NH_4^+/dm^3$]	COD [mg O_2/dm^3]	Suspension [mg/dm^3]
Sludge liquids separated from non-sonicated, digested sludge treated with different coagulants							
Crude sludge liquids	—	6.76	24.3	7.94	931.5	784	280
PIX 113	4.5	5.97	14.7	4.81	927.3	387	620
	5.0	5.76	4.2	1.38	836.9	134.4	600
	5.5	5.57	1.5	0.49	792.7	78.4	500
PIX 113 (4.5) + Zetag 8160*	1.5	6.20	4.1	1.35	887	580	580
	2.5	5.94	3.7	1.21	843	545	520
	3.5	5.70	3.0	1.00	824	510	460

* Sludge liquid obtained from non-sonicated, digested sewage sludge first treated with 4.5 mg/g d.m. of PIX 113, and then with different doses of Zetag 8160: 1.5; 2.5; 3.5 mg/g d.m.

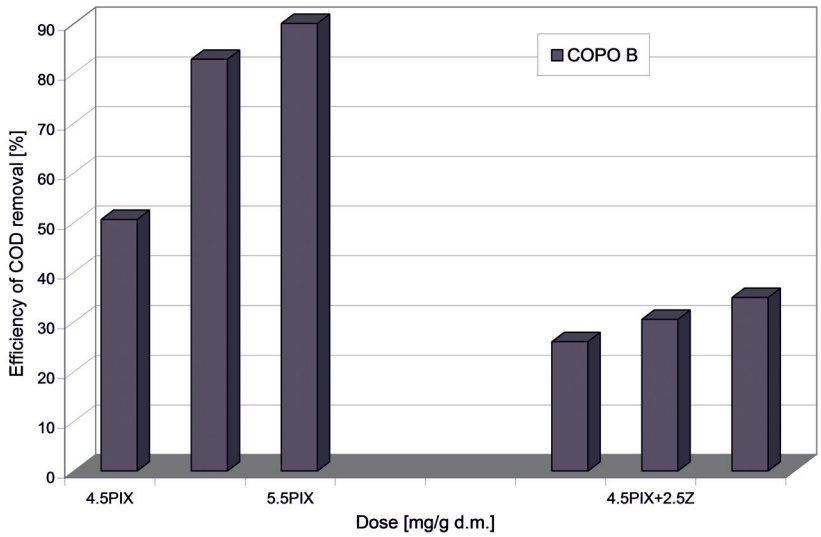

Fig. 3. Efficiency of COD removal in relation to dose and type of coagulant (COPO B – sludge liquid from digested sludge B)

The amount of organic compounds (COD) in sludge liquids decreased during the process of sewage sludge conditioning. The efficiency of their removal grew with the growing dose in the case of PIX 113 and the method combining 4.5 mg/g d.m. of PIX 113 and different doses of Zetag 8160 (Fig. 3). The best effect of organic compounds removal was observed for the liquid separated from sludge B treated with PIX 113: between 50.6% and 90%. In the combined method the reduction of organic compounds amount was between 26% and 34.9%.

Conclusions

1. After mechanical dewatering, sludge liquid was highly contaminated.
2. The reagents and ultrasonic field used to condition the sludge before mechanical dewatering caused the reduction of contamination in the lechates in relation to crude sludge liquids.
3. The combined effect of inorganic coagulant PIX 123 and Zetag 8160 polyelectrolyte allowed the reduction of total suspended solids amount in sludge liquids. The best effect was achieved when using PIX 123. It was 53.8%. The use of the PIX 113 coagulant and Zetag 8160 polyelectrolyte initially increased the ratio of total suspended solids in relation to crude sludge liquids, and then the amount of suspended solids decreased with the increasing dose of conditioning chemicals.
4. The best effect of organic compounds removal was observed for the liquid from sonicated sludge treated with PIX 123 (76.7%) and the combined method (52.1%). In the liquid from non-sonicated sludge the use of PIX 113 coagulant led to reducing the COD value to 90%, and in the combined method, to 26%.

5. In lechates from the dewatering of non-sonicated sludge treated with PIX 113 the amount of ammonium nitrogen was reduced to 14.5%, and phosphates to 93.8%, in relation to crude sludge liquids.

6. Zetag 8160 polyelectrolyte proved to be the least effective in reducing contamination in sludge liquids.

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JAKOŚĆ CIECZY OSADOWYCH POWSTAJĄCYCH W PROCESIE MECHANICZNEGO ODWADNIANIA OSADÓW PRZEFERMENTOWANYCH

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Abstrakt: Jakość cieczy osadowych powstających w procesach mechanicznego odwadniania osadów zależy od technologii stabilizacji oraz rodzaju urządzenia, prawidłowej jego pracy oraz właściwego doboru środków chemicznych do kondycjonowania. W artykule przedstawiono wpływ wybranych środków i metod kondycjonowania, takich jak: PIX 113, PIX 123, polielektrolit Zetag 8160, pole ultradźwiękowe oraz łączne ich działanie na właściwości cieczy osadowych. Surowe ciecze osadowe charakteryzowały się wysokimi stężeniami azotu amonowego (931,5–1508,9 mg $N\text{-}NH_4^+/dm^3$), fosforanów (24,3–89,4 mg PO_4^{3-}/dm^3) oraz związków organicznych oznaczonych jako ChZT (784,0–1856 mg O_2/dm^3). Stwierdzono, że połączone działanie nieorganicznego koagulantu PIX 123 i polielektrolitu pozwoliło na zmniejszenie ilości zawiesin oraz ChZT w cieczach osadowych. W przypadku zawiesiny najlepszy stopień jej zmniejszenia uzyskano przy stosowaniu PIX-u 123. Wynosił on 53,8%. Analizując zmiany ChZT, podobne efekty uzyskano dla PIX-u 123 (43%) oraz metody łączonej (41,6%). Natomiast użycie koagulantu PIX 113 i polielektrolitu Zetag 8160 spowodowało w cieczy osadowej zwiększenie zawiesin ogólnych w odniesieniu do surowych cieczy osadowych. Działanie koagulantu PIX 113 wpłynęło na zmniejszenie wartości ChZT (90%), azotu amonowego (14,9%) i fosforanów (93,8%) w odniesieniu do surowych cieczy osadowych. Najmniej skuteczny okazał się polielektrolit Zetag 8160.

Słowa kluczowe: ciecze osadowe, koagulanty, polielektrolity, pole ultradźwiękowe, mechaniczne odwadnianie

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BIOAVAILABILITY OF HEAVY METALS IN THE MUNICIPAL SEWAGE SLUDGE

BIODOSTĘPNOŚĆ METALI CIĘŻKICH W KOMUNALNYCH OSADACH ŚCIEKOWYCH

Abstract: Usually chemical form of metal is considered as the most important factor influencing its mobility and bioavailability. In order to determine forms of heavy metals in sewage sludge the speciation analysis is used. The analysis is based on sequential extraction of metals with increasingly aggressive solvents. Reagents chosen for each step extract metal groups with specified properties. The four steps extraction (BCR) gained wide recognition. It extracts metals in following groups: I – exchangeable and associated with carbonates, II – associated with hydrated iron oxides and manganese oxides, III – associated with organic matter, IV – metals that can be found in the residual fraction. Metals found in the first fraction (exchangeable and carbonate) are believed to be mobile. The release of those metals can occur with change in pH or in ionic composition of liquid. Metals bound to hydrated forms of iron and manganese oxides and to organic matter are also available. The fraction of iron and manganese oxides is sensitive to redox changes, whereas metals bound to organic matter are released during mineralization of the substrate. Metals considered to be immobilized are those that can be found only in the residue, which dissolves only in concentrated mineral acids. The speciation analysis of heavy metals in stabilized sewage sludge gives information important for determination of the rate at which heavy metals pass into soil solution and also, as a consequence, their uptake by plants. This information is especially important when considering agricultural usage of sludge.

The purpose of presented studies was compare the amount of metals potentially available for plants with their content in chemicals forms detected with sequential extraction procedure and evaluation the hypothesis that content of metals in some fractions could be equivalent to their bioavailability

The report presents results of BCR sequential extraction procedure of metals (Zn, Cu, Ni, Cd, Pb) from sewage sludge from two WWTP and single extraction with 1 M HCl used for determination of bioavailable forms of metals.

Our studies stated the presence of copper and cadmium generally in the organic fraction, nickel and lead in the residual fraction and zinc both in the organic as well as in the iron and manganese oxyhydroxides fraction. However determined bioavailability significantly differed from the metals content in the fractions regarded as mobile.

Content of zinc in the I and II fraction was on the level 48–51% of the total amount and bioavailability 86–92%. Concentration of copper and nickel in the mobile fractions (I and II) was 2–4% and 22–33%,

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respectively and in bioavailable form 49–63% and 25–41%, respectively. Lead available content in sludge was in the same scheme like copper and nickel (21–22 and 51–62%, respectively).

Bioavailable content detected for analysed metals covered I and II mobile fractions but for Zn, Cu and Ni also significant part of III – potentially immobile fraction. Additionally for Pb even a part of IV – assumed as practically immobile and inactive fraction. Obtained data indicated that speciation forms of metal are not always equivalent to their bioavailability.

Keywords: heavy metals, municipal sewage sludge, bioavailability, four steps extraction BCR procedure, BCR sequential extraction

1. Introduction

The anthropogenic human activities causes production of excess sewage sludge, which proper disposal become more and more urgent. The high content of organic matter and nutrient elements indicates natural application of sludge as fertilizer or regenerator for soil. However, sewage sludge being the final waste material of communal and industrial wastewater treatment processes usually contains transition metals (heavy metals), sometimes on relatively high level and the disposal of such material could result in secondary environmental pollution and is a growing environment problem. The utilization of sewage sludge would be restricted by the presence of heavy metals compounds. Direct disposal or agricultural application of hazardous sewage sludge containing heavy metals may cause serious soil and underground water pollution problems. The environmental impact of sewage sludge contamination depends not only on the total amount of metals but mainly on their mobility and bioavailability which are influenced by their leaching and interactions with all components of the ecosystem [1–3].

Sewage sludge used in nature and agricultural purposes, besides sanitary requirements, have to characterize for acceptable content of heavy metals. Usually, in the stabilized and dewatered sewage sludge the highest content of zinc is observed. Relatively great content of copper and in some cases high concentration of chromium and lead are determined [4–7]. Transfer of heavy metals from sewage sludge to the food chain is done by plants cultivated on soil fertilized with these sludge. Although trace quantities of some heavy metals (as microelements) are necessary in the process of the metabolism of plants and animals, they are able accumulate to phytotoxic levels in organisms and the excessive amounts of them could have the toxic action and stand danger both for plants, animals, as well as human [8–12].

The mobility and bioavailability of heavy metals are determined by the chemical form of them. Detection of bioavailable fraction and evaluation migration possibilities of heavy metals associated with solid phase is done with single extraction process. However to obtain information allowing the recognition of forms of metal presence, their origin sources, the way of association to solid matrix components, possibilities of the mobilization and transport the sequential multistep extraction procedures are performed [13]. Sequential extraction procedure is realized with increasingly aggressive solutions of substances. For each step there is selected reagent possible to eluate the group of metals compounds with strictly known properties. Procedure initially proposed by Tessier [14] was modified and as a result of work of many groups of researches in

framework of Standards, Measurements and Testing Programme of the European Union Commission [15] a shortened, three – step extraction was accepted. The procedure is known as BCR procedure (from the earlier name of this commission: Community Bureau of Reference).

BCR procedure determines the following groups of metals: I – acid soluble, II – reducible (associated with hydrated Fe and Mn oxides), III – oxidizable (associated with organic matter and sulfides) and IV – residual [16–18]. Metals detected in two former fractions are believed to be mobile and bioavailable. The bounds for metals in two latter fractions are much stronger and metals are considered to be potentially immobile and inaccessible. The residual fraction is considered to be chemically stable and biologically inactive. Metals found in this fraction are not harmful to the aquatic ecosystem. The most mobile, meaning easily dissolved in the soil solution and assimilated by plants, are considered to be acid soluble metals.

Actually there are not uniform procedures for determination of heavy metals bioavailability in sewage sludge used in agriculture. For that purpose, extraction techniques developed for soil are being adopted [18]. The used single step extraction with acids, neutral salts or chelating agents could indicate possibility of transfer of heavy metal from sludge to soil solution and finally to plant, animal and human organisms.

The purpose of presented studies was compare the amount of metals potentially available for plants with their content in chemicals forms detected with sequential extraction procedure and evaluation the hypothesis that content of metals in some fractions could be equivalent to their bioavailability.

2. Material and methods

The analysed material was final, dewatered sewage sludge after hydraulic press station. Sewage sludge samples were taken from two waste water treatment plants in central Poland in autumn 2016. Wastewater treatment plant located in A, with capacity of 9200 m^3 per day, is being conducted by means of activated sludge method, with the use of nitrification, denitrification and biological dephosphatation processes. Wastewater treatment plant located in B, with capacity of 20000 m^3 per day, is being conducted by means of activated sludge with nitrification, denitrification and chemical dephosphatation.

Properties of sludge samples, like hydration, total solids, volatile solids concentration (gravimetric method) were determined.

The samples were initially air-dried under laboratory condition (temperature about 20^{o}C), next dried at 105^{o}C in dryer. Then sludge samples were homogenized in an agate mortar and passed through a stainless sieve with 0.4 mm diameter meshes and kept in plastic container for further analyses. Three different samples of the same sludge were prepared for the analyses. Presented results are the mean values from triplicate measurements.

Sequential extraction was carried out according to the BCR procedure in order to quantify the chemical forms of heavy metals in the sludge samples – Table 1 [16].

Table 1

Sequential extraction procedure, BCR, per 1g of dry matter of sewage sludge

Step	Reagent	Temperature [°C]	Time [h]	Fraction	Nominal target phase(s)
1	40 cm^3 0.11 M CH_3COOH	22	16	Exchangeable, acid soluble	Soil solution, exchangeable cations, carbonates
2	40 cm^3 0.5 M $NH_2OH \cdot HCl$ (pH 2)	22	16	Reducible	Iron and manganese oxyhydroxides
3	10 cm^3 8.8 M H_2O_2 (pH 2–3)	22	1	Oxidizable	Organic matter and sulfides
	—	85	1		
	10 cm^3 8.8 M H_2O_2 (pH 2–3)	85	1		
	50 cm^3 1 M CH_3COONH_4	22	16		
4	2 cm^3 HNO_3 (65%) 6 cm^3 HCl (37%)	120	2	Residual	Silicate minerals

Total content of selected heavy metals (Zn, Cu, Ni, Cd and Pb) was studied after sample mineralization at 120°C with mixture of concentrated acids: HNO_3 and HCl (1 + 3 – aqua regia) for 2 hours.

The bioavailable metal content was analyzed according to procedure proposed for soil [20] with single extraction with 1 M HCl for 1 hour at 20°C.

The contents of studied metals after mineralization, sequential analysis as well as single step extraction with 1 M HCl were detected by an atomic absorption spectrometry method (spectrometer novAA 400, Analytic Jena, Germany).

3. Results and discussion

Analysed sewage sludge samples characterized by hydration and organic matter content equal to 81% and 78%, respectively, for the sewage sludge collected in wastewater treatment plant located in A and 85% and 62%, respectively for the sludge from wastewater treatment plant located in B.

Content of heavy metals (average value) and their percentage distribution over the fractions of sewage sludge (A) and (B) as well as potential bioavailability are presented in Table 2.

Analysed sewage sludge, on account of total heavy metals content (zinc, copper, nickel, lead and cadmium) was in agreement with legislative requirements for sewage sludge used in agriculture, for land reclamation to agricultural and non-agricultural purposes. Despite the total content of heavy metal is useful detector of environmental contamination, it does not provide enough information about potential environmental impact. More detailed data is obtained from single or multi – step extraction procedures indicating mobility and bioavailability of heavy metals [19, 21, 22].

Table 2

Chemical fraction, total and bioavailable content of heavy metals in sewage sludge A and B

Fraction	Zn		Cu		Ni		Cd		Pb	
	[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]	[mg /kg]	[%]	[mg/kg]	[%]
Sewage sludge A										
I	102.4 ± 0.9	13.3	2.1 ± 0.2	1.8	4.5 ± 0.2	11.7	0.3 ± 0.1	9.4	5.1 ± 0.2	11.9
II	291.7 ± 1.7	37.8	2.2 ± 0.1	1.9	4.0 ± 0.1	10.4	0.9 ± 0.2	28.1	4.3 ± 0.1	10.1
III	354.1 ± 2.6	45.9	101.6 ± 0.7	89.2	7.9 ± 0.2	20.5	1.4 ± 0.1	43.8	12.3 ± 0.3	28.7
IV	22.7 ± 0.4	3.0	8.0 ± 0.3	7.0	22.1 ± 0.4	57.4	0.6 ± 0.1	18.8	21.1 ± 0.5	49.3
Sum	770.9	100.0	113.9	100.0	38.5	100.0	3.2	100.0	42.7	100.0
BAV	665.9 ± 3.8	86.4	71.8 ± 0.5	63.0	9.6 ± 0.2	24.9	1.3 ± 0.3	40.6	21.9 ± 0.5	51.3
Total	876.0 ± 4.2	—	123.7 ± 1.1	—	34.8 ± 0.7	—	3.0 ± 0.3	—	36.0 ± 0.3	—
Sewage sludge B										
I	229.8 ± 2.1	12.9	1.8 ± 0.1	0.9	10.0 ± 0.3	22.9	1.0 ± 0.1	17.2	10.4 ± 0.2	10.3
II	622.5 ± 3.3	34.8	2.1 ± 0.1	1.0	4.6 ± 0.2	10.5	0.8 ± 0.1	13.8	9.8 ± 0.2	9.8
III	827.6 ± 4.4	46.3	181.5 ± 1.5	86.9	10.1 ± 0.2	23.1	2.9 ± 0.2	50.0	9.2 ± 0.2	9.2
IV	108.3 ± 0.8	6.0	23.5 ± 0.4	11.2	19.0 ± 0.3	43.5	1.1 ± 0.1	19.0	71.0 ± 0.6	70.7
Sum	1788.2	100.0	208.9	100.0	43.7	100.0	5.8	100.0	100.4	100.0
BAV	1645.7 ± 5.1	92.0	102.3 ± 1.1	49.0	18.0 ± 0.3	41.2	2.2 ± 0.2	37.9	62.8 ± 0.4	62.5
Total	2044.0 ± 6.9	—	195.8 ± 1.7	—	39.1 ± 0.5	—	4.7 ± 0.2	—	85.0 ± 0.6	—

I, II, III, IV – chemical fraction according to BCR procedure; BAV – bioavailable content of metal.

The content of zinc in both sewage sludge was the highest: 876 and 2044 mg/kg d.m. (dry matter) for A and B samples, respectively. The mentioned metal was the mostly bounded to III and II fraction. Organic matter and sulfides as well as Fe and Mn hydroxides fractions were previously reported as typical for zinc [23].

Copper, lead and nickel total contents were significantly lower and in sewage sludge A were equal to 124, 36 and 35 mg/kg d.m., respectively and in sewage sludge B: 196, 85 and 39 mg/kg d.m. Higher contents of copper were detected in organic matter and sulfides fraction, lead and nickel in residual fraction.

Cadmium characterized the lowest total content on the level: 3.0 and 4.7 mg/kg d.m. for A and B samples, respectively. The highest content of cadmium was detected in Fe and Mn hydroxides fraction. Similar affinity of metals to particular fraction was confirmed by another authors [24, 25].

Dominant role of sewage sludge organic-sulfide fraction in binding zinc, copper, and cadmium, was confirmed by Fuentes et al [26], Stylianou et al [27], Hanay et al [28]. In case of zinc large amount of this metal was found also in iron and manganese oxide fraction, in case of nickel and cadmium – in sludge exchangeable-carbonate fraction. Strong zinc affiliation by iron and manganese oxides in sewage sludge was pointed out by Walter et al [29], Chen et al [24], Jamali et al [25] whereas high concentration of nickel in sludge exchangeable-carbonate fraction was stated by Hanay et al [28], Lasheen and Ammar [30].

The analyses of the sludge indicated low concentration of zinc and cooper in the insoluble fraction (3–11%). The content of lead and nickel in this fraction was 49–71%; 44–57%, respectively. The residual fraction is considered to be chemically stable and biologically inactive. Metals that were found in this fraction are not harmful to aquatic and soil ecosystems. On the other hand in the exchangeable-carbonate fraction, most mobile fraction of metals, the highest concentration of nickel (12–23%) was found. The presence of high concentration of nickel in the mobile fraction indicates that when the outer conditions like: equilibrium in the sorption-desorption system change or pH decrease, the release of metal ions into the soil-water environment can occur. For other metals: zinc, copper, cadmium and lead, their content in the exchangeable-carbonate fraction was 13%; 1–2%; 9–17%; 10–12%, respectively.

Content of metals with distribution over particular sludge fractions with comparison to their potential bioavailability for both types of analyzed sludge samples are presented on Figs. 1–5.

Zinc content in sewage sludge A as well as sludge B corresponded to mobile I and II fraction and additionally to almost all III fraction, commonly called potentially immobile (Fig. 1). Content of zinc in the I and II fraction was on the level 48–51% of the total amount and bioavailability 86–92%. The report of Rajmund and Bozym [19] demonstrated that acidic 1M solution of HCl was the strong but not selective extrahent. It eluate metals bounded to exchangeable, carbonate, iron and manganese oxides as well as with organic matter. The results indicated that mobility and bioavailability could not be considered as parallel and similar parameters. In the last years a number of studies have been done to project and validate methods of measure or predict content of bioavailable forms of metals. Depending on the type of methods used, strength of

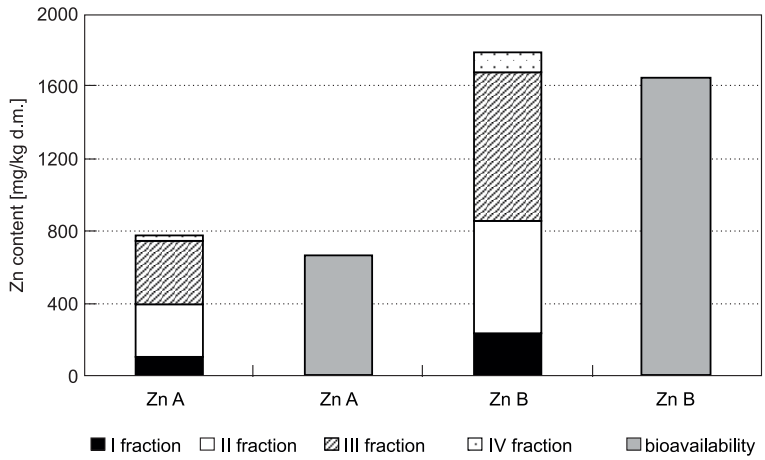

Fig. 1. Chemical fractions and bioavailable content of Zn in analysed sewage sludge samples A and B

extraction solution, variable results could be obtained for selected metal with specific properties. Generally for mobile metals, solutions of neutral salts are recommended for determination of bioavailable forms. For relatively low mobile metals, strongly bounded to solid matrix, extraction with strong acid or chelating agent solution should be selected. For routine analysis usually simple extraction with neutral salt or strong acid is presently proposed [22].

Similar behaviour was observed for copper (Fig. 2) and nickel (Fig. 3). Potentially available for plants content of metals covered not only mobile I and II fraction, but also practically immobile III fraction of metals in sludge A and B. Concentration of copper and nickel in the mobile fractions (I and II) was 2–4% and 22–33%, respectively and in bioavailable form 49–63% and 25–41%, respectively.

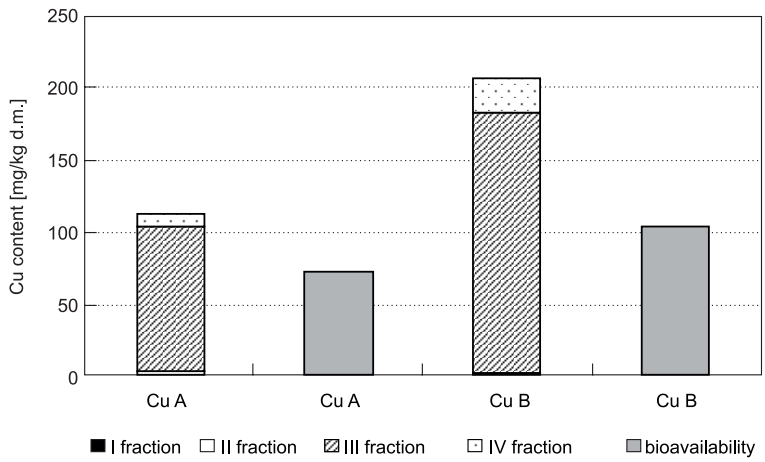

Fig. 2. Chemical fractions and bioavailable content of Cu in analysed sewage sludge samples A and B

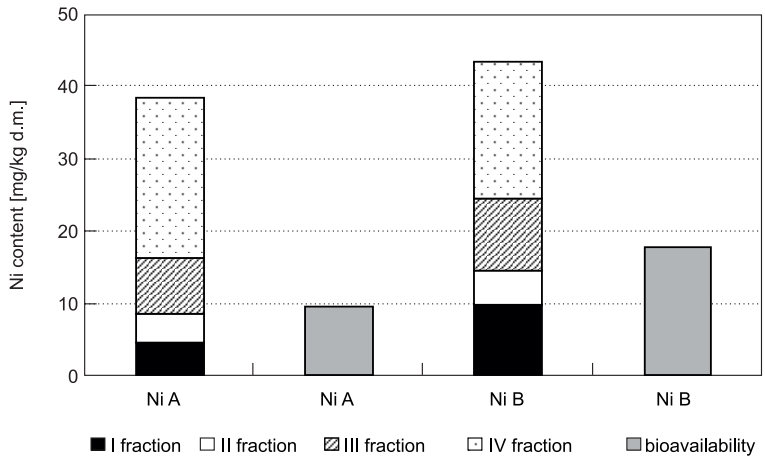

Fig. 3. Chemical fractions and bioavailable content of Ni in analysed sewage sludge samples A and B

Lead available content in sludge A was in the same scheme like copper and nickel (22 and 51%, respectively). A little bit different behaviour of Pb was in sludge sample B (Fig. 4). Its bioavailability covered all I, II and III fraction and significant part of residual fraction, usually considered as immobile and inactive environmentally fraction.

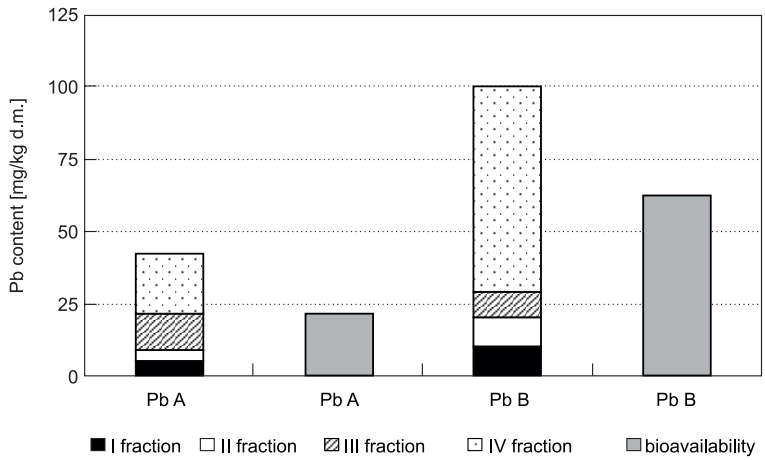

Fig. 4. Chemical fractions and bioavailable content of Pb in analysed sewage sludge samples A and B

Cadmium behaviour was in agreement with typical approach that first two fraction of metals in sewage sludge are equivalent to metal bioavailability (Fig. 5). Content of metal assumed as bioavailable covered in practise only I and II fraction (31–41%).

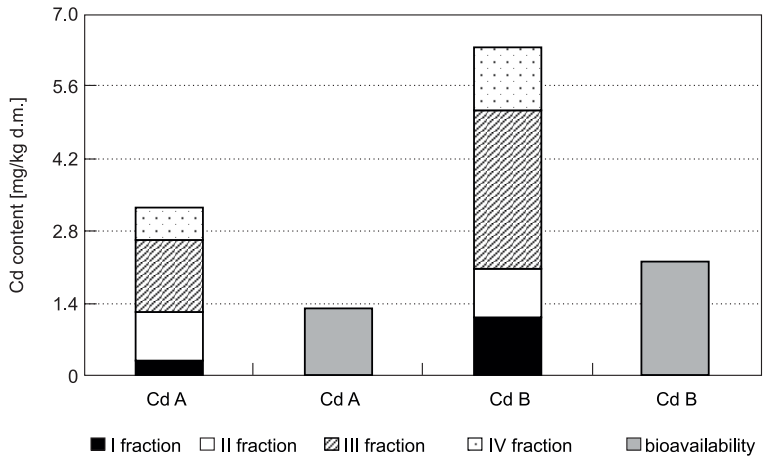

Fig. 5. Chemical fractions and bioavailable content of Cd in analysed sewage sludge samples A and B

4. Conclusions

Our studies stated the presence of copper and cadmium generally in the organic fraction, nickel and lead in the residual fraction and zinc both in the organic as well as in the iron and manganese oxyhydroxides fraction. It was detected that heavy metals mobility (content in the exchangeable, carbonate and iron and manganese oxy-hydroxides fractions) changed in the order: Zn > Cd > Ni > Pb > Cu. However determined bioavailability significantly differed from the metals content in the fractions regarded as mobile. Results obtained after washing of metals with 1M HCl allowed the ordering of metals with decreasing bioavailability: Zn > Pb ~ Cu > Cd > Ni. The extraction of metals from sewage sludge samples with mentioned above solution was in the range from 25 to 92%. Similar values of bioavailable content of metals were reported previously [19].

It could be concluded that metals mobility, bioavailability and content in given fractions detected in sequential extraction procedure are not equivalent and mentioned parameters have to be analysed separately.

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BIODOSTĘPNOŚĆ METALI CIĘŻKICH W KOMUNALNYCH OSADACH ŚCIEKOWYCH

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Abstrakt: O mobilności i biodostępności metali ciężkich decyduje przede wszystkim forma chemiczna ich występowania. W celu określenia form metali wykonuje się analizę specjacyjną opartą na ekstrakcji sekwencyjnej, która polega na stopniowym wydzielaniu metali z osadów roztworami o wzrastającej agresywności. Do każdego etapu dobiera się reagenty, które są zdolne wyekstrahować grupę połączeń metali o znanych właściwościach. Szerokie uznanie zdobyła czterostopniowa ekstrakcja (BCR), której zastosowanie umożliwia wydzielenie metali: I – wymienialnych i związanych z węglanami, II – związanych z uwodnionymi tlenkami żelaza i manganu, III – z materią organiczną oraz IV – pozostałych. Za mobilne uważa się metale występujące w pierwszej frakcji (wymiennej i węglanowej), z której ich uwalnianie następuje pod wpływem zmiany pH, składu jonowego cieczy. Także metale związane z uwodnionymi tlenkami żelaza i manganu oraz z materią organiczną są dostępne. Frakcja tlenków żelaza i manganu jest wrażliwa na zmiany potencjału redox, natomiast metale związane z substancją organiczną są uwalniane w procesie mineralizacji tego substratu. Za metale unieruchomione uważa się te, które są zgromadzone w pozostałości rozpuszczalnej dopiero w stężonych kwasach mineralnych. Wykonanie analizy specjacyjnej metali ciężkich w ustabilizowanych osadach ściekowych jest szczególnie istotne przy rolniczym wykorzystaniu osadów, pozwala bowiem ocenić szybkość przechodzenia metali do roztworu glebowego, a w efekcie ich pobranie przez rośliny.

Celem przedstawionych badań było porównanie ilości metali potencjalnie dostępnych dla roślin z ich zawartością w formach chemicznych oznaczonych w sekwencyjnej procedurze ekstrakcyjnej i ocena hipotezy, że zawartość metali w niektórych frakcjach może być równoważna biodostępności.

W celu oznaczenia form metali ciężkich (Zn, Cu, Ni, Cd, Pb) w osadach ściekowych pobranych z dwóch mechaniczno-biologicznych oczyszczalni ścieków zastosowano ekstrakcję sekwencyjną BCR, natomiast do oznaczenia biodostępnych form metali pojedynczą ekstrakcję 1 M HCl.

Badania potwierdziły występowanie miedzi i kadmu głównie we frakcji organicznej, niklu i ołowiu we frakcji pozostałościowej, natomiast cynku zarówno we frakcji oragnicznej, jak i tlenków żelaza i manganu.

Natomiast oceniona biodostępność znacznie się różniła od występowania metali we frakcjach uważanych za mobilne.

Zawartość cynku we frakcji I i II wynosiła 48–51% całkowitej ilości, natomiast biodostępność 86–92%. Zawartość miedzi, niklu i ołowiu w formach mobilnych (I i II) wyniosła odpowiednio 2–4%; 22–33% i 21–22%, natomiast w biodostępnych odpowiednio 49–63%; 25–41% i 51–62%.

Biodostępna zawartość analizowanych metali została oznaczona we frakcji I i II, ale dla Zn, Cu i Ni, również w znaczącej ilości we frakcji III – potencjalnie mobilnej. W przypadku Pb biodostępność dotyczyła także części frakcji IV – przyjętej jako praktycznie niemobilnej. Uzyskane dane wskazywały, że formy chemiczne metali uznane jako mobilne nie są zawsze równoznaczne formom biodostępnym.

Słowa kluczowe: metale ciężkie, komunalne osady ściekowe, biodostępność, czterostopniowa procedura ekstrakcji BCR, ekstrakcja sekwencyjna BCR, BCR

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CO-DIGESTION OF SEWAGE SLUDGE AND GLYCEROL FRACTION MIXTURE FACILITATED BY MICROWAVE PRETREATMENT

KOFERMENTACJA MIESZANINY OSADÓW ŚCIEKOWYCH I FRAKCJI GLICERYNOWEJ WSPOMAGANA PROMIENIOWANIEM MIKROFALOWYM

Abstract: In the present study, the concept of integrated technological co-digestion system that ensures high effectiveness of glycerine fraction and sewage sludge was developed. The addition of glycerol fraction to sewage sludge influenced positively the degree of organic matter biodegradation and the quantity and quality of biogas produced. Introducing sewage sludge after effective microwave disintegration into feedstock allowed to further improve the effectiveness of the co-digestion process analysed. The co-digestion mixtures performed in conditions ensuring high effectiveness and an appropriate digestion stability (hydraulic retention time (HRT) = 20 days) allowed to increase the methane production by 18–23% and methane yield up to 10% compared to the samples of glycerine and untreated sludge digested in optimal conditions (HRT = 22–24 days). However, it should also be taken into consideration that initial sludge pre-treatment allowed to decrease the HRT value by at least 2 days.

Keywords: co-digestion, glycerol fraction, biodiesel, microwave pre-treatment, sewage sludge

Introduction

The scarcity of fossil fuels, growing emissions of combustion-generated pollutants, and their increasing costs, have made alternative fuel sources more attractive. Biodiesel (fatty acid methyl esters) produced by the process of transesterification of vegetable oils

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or animal fats with methanol are potential substitutes for petroleum-based diesel fuels. Compared to conventional diesel, biodiesel is biodegradable, renewable, non-toxic, and has low pollutant emissions (especially SO_x) [1]. However, biodiesel production generates by-products; including oilcake resulting from the extraction of oil and glycerol fraction generated at the stage of esterification of oil. During the processing of 1000 kg of rape, cake of about 650 kg and about 100 kg glycerol phase are obtained [2]. Oil cakes are mostly utilized as a component of animal feed. Whilst, the research is carried out in the direction of their usage as feedstock in the process of pyrolysis, for the bio-oil and bio-char generation. These substances can be used as substrates for the production of enzymes, antibiotics, etc. [3]. The glycerol fraction, the second by-product, can be assigned to one of three categories based on its purity. Raw glycerol contains up to 63.3% of glycerol, up to 26.8% of water, and approximately 26.7% of methanol. In addition, it contains organic substances (FAME) and potassium and sodium salts. Glycerol of average purity (technical glycerol) contains approximately 80% of glycerol and much lower percentages of water and methanol. Glycerol of the highest purity (> 99.8%) is received in glycerol distillation plants. In the largest biodiesel production plants, methanol is evaporated from the glycerol fraction, and the free fatty acids are purified away, producing technical glycerol of ~80% purity. If technical glycerol is collected and purified up to 99.8%, this generates additional costs connected with energy and materials. In principle, the demand for it is limited because of a large surplus in the market. Thus, new possible uses of technical, *ie* non-purified glycerol are highly desirable [4]. One of the most attractive ones is to use the liquid fuel in various combustion plants. However, glycerol has quite a high auto-ignition temperature (370^oC) compared to other liquid fuels. Moreover, when glycerol is heated above 280^oC, toxic acrolein is produced [5, 6]. As glycerol is highly flammable and combusts at a higher temperature, a high temperature should be maintained in glycerol combustion processes. Other options include the production of fuel emulsions using raw or technical glycerol. However, the use of this fuel in boilers is currently limited because of its high sulphur content [5, 6]. Another possible applications of glycerol include: pharmaceuticals, cosmetics and plastics production. For example, 1,3-propanediol is produced microbiologically from glycerol. The latter product can substitute toxic ethylene glycol used for polyesters production [7]. However, in order to obtain high quality of glycerol, – depending on the presence of impurities therein, it is necessary to highly pretreat raw glycerol fraction after biodiesel production, which is not always economically justified. In practice, glycerol fraction similarly to rapeseed cakes constitutes very frequently the component of animal feed. Considering its high content of easily biodegradable ingredients (80–90%), anaerobic digestion of glycerol for biogas production constitutes an interesting alternative. However, glycerol direct utilization as the only substrate in the fermentation processes is very limited due to lack of nitrogen, which is necessary to ensure the sufficient activity of microorganisms involved in the biochemical processes. The problem can be solved by glycerol co-digestion with other co-substrates, *eg* waste sewage sludge [8]. However, due to the complex structure of waste activated sludge (WAS), it is difficult to achieve high effectiveness of the sludge undergoing biodegradation in anaerobic conditions. The

problem can be solved by the application of effective sludge pre-treatment, *eg* by microwave irradiation, – which is considered now as very novel method. The sludge contains a high proportion of water and thus easily absorbs microwave irradiation and the mechanism of microwave irradiation includes "thermal" and so-called "non-thermal" effects. The positive effects of sludge pre-treatment by means of microwave irradiation have recently been widely reported in the literature [9–12]. However, the cases mainly focus on the determination of optimal pre-treatment conditions and/or assessment of its advantages over traditional thermal pre-treatment method. The research aimed at subsequent anaerobic digestion of treated sludge together with other co-substrates is very scarce. What is more, according to our knowledge, there is no reports on enhancement of continuous co-digestion process (surplus activated sludge and non-purified glycerol fraction), by the microwave irradiation. The aim of the study was to develop the concept of integrated technological system that ensures high effectiveness of waste glycerol (technical glycerol) and sludge anaerobic co-digestion. The present study is focused on the assessment of microwave irradiation as the effective means of enhancing the anaerobic digestion (AD) effectiveness of the analysed co-digestion mixtures. The anaerobic digestion processes encompassed batch and continuous modes. The purpose of the former process was to determine the optimal proportion of waste glycerol, which can be added to the mesophilic digestion of sludge without significant deterioration of the stability of the process. Whilst, the latter process (continuous mode) allowed to determine the most appropriate parameters of the process, *ie* organic loading of the bioreactor and hydraulic retention time (HRT) of the optimal co-digested mixture.

Materials and methods

Feedstock of anaerobic digestion

Samples of surplus activated sludge (SAS) were taken from an Enhanced Biological Nutrient Removal (EBNR) full-scale municipal sewage treatment plant in Silesia region; Poland. The treatment plant was designed for nutrients removal. With the intention of phosphorous and nitrogen compounds removal, anaerobic, anoxic and aerobic sectors have been distinguished. The plant was designed for a flow of 120 000 m^3/day. At present the amount of treated wastewater is about 90 000 m^3/day. Solid retention time (SRT) is about 14 days and concentration of mixed liquid suspended solid (MLSS) 4320–4640 mg/dm^3. Surplus activated sludge samples were collected immediately after the compaction process (using a belt compactors) (Table 1). The by-product after biodiesel production (technical glycerol) named so "glycerol fraction" in this paper, was used as a co-substrate of anaerobic digestion. The glycerin was obtained from a local biorafinery (Silesian province, Poland). The characteristics of the glycerol fraction is shown in Table 1. Co-digestion trials were inoculated using digested sludge; from the same plant which provided samples of surplus activated sludge (Table 1).

Table 1

Characteristics of co-substrates and inoculum used for anaerobic digestion

Indicator	Unit	Untreated sludge[a]	Pretreated sludge[b]	Digested sludge	Glycerine fraction
pH	[-]	6.4 (0.4)*	6.2 (0.2)	7.3 (0.2)	5.2 (0.3)
Total solids (TS)	[g/dm^3]	51.6 (3.4)	52.9 (2.5)	34.3 (0.4)	783 (7)
Volatile solids (VS)	[g/dm^3]	35.1 (2.7)	36.2 (2.1)	19.3 (0.3)	770 (7)
Soluble chemical oxygen demand (SCOD)	[g/dm^3]	0.27 (0.10)	6.10 (0.45)	1.64 (0.21)	—
C_{org}	[% TSS]	33.0 (0.5)	33.5 (0.4)	31.0 (0.9)	46.7 (0.7)
Total Kjeldahl nitrogen (TKN)	[% TSS]	5.01 (0.36)	4.89 (0.25)	3.27 (0.03)	0.61 (0.01)
NH_4^+	[mg/dm^3]	15.8 (5.9)	115 (10)	1650 (110)	254 (25)
PO_4^{3-}	[mg/dm^3]	144 (35)	695 (25)	240 (60)	—
Volatile fatty acids (VFA)	[mg/dm^3]	83 (20)	125 (25)	870 (26)	—
Alkalinity	[mg $CaCO_3$/dm^3]	1161 (104)	1085 (95)	5845 (346)	—

* () – standard deviation, [a] surplus activated sludge without pretreatment, [b] surplus activated sludge after effective pre-treatment by microwave irradiation [13].

Microwave sludge pre-treatment

The most appropriate technological conditions of sewage sludge pretreatment (exposure time, sludge final temperature, microwave power) as factors ensuring an efficient sludge lysis, has been established previously. The process of sewage sludge disintegration by the microwave irradiation led to the effective destruction of flocks, which was confirmed by an increase in the organic content (SCOD, soluble proteins), mineral substances (NH_4^+, PO_4^{3-}) in the liquid sludge phase as well as an increase in biogas production [13]. Based on our previous studies on microwave excessive sludge disintegration (SASMD), the sludge pretreated exposed to the action of microwaves for 2.0 minutes and resulting in the sludge temperature of about 70^{o}C, – was used in the present study. There was no influence of microwave power applied in the range of 700–1200 W – on the effectiveness of the sludge pretreatment. The microwave power of 1200 W was used in the present study, as it turned out to be the less energy demanding [13, 14].

Anaerobic digestion in batch and continuous mode

Anaerobic digestion (co-digestion) in mesophilic conditions (36 ± 1)^{o}C was performed under batch and continuous conditions. The first of these processes was conducted in order to determine the most favorable proportion of technical glycerol in the co-digestion mixtures (glycerol + sewage sludge); providing a high efficiency and stability of the anaerobic digestion. The content of waste glycerine in co-digestion mixtures amounted to between 1–5% (by weight). During the continuous co-digestion process, the influence of the hydraulic retention time (HRT) of the co-digestion (the most favorable) mixture on the effectiveness and stability of the process was analysed.

The batch tests were performed in 1 dm^3 bottles (0.5 dm^3 of working volume). The co-digestion mixtures were inoculated with fermented sludge. The proportion of inoculum amounted to 50% of total working volume. Digestion mixtures were enriched with nutrients [15]. Mixtures containing only nutrients and inoculum were used as controls. Assays were performed at (36 ± 1)^{o}C for a period of 25 days. The amount of methane produced was expressed per unit of initial organic matter – volatile solids (VS) – in the feedstock. Methane produced by inocula (control samples) was subtracted from the amount of methane produced in all tested assays. The digestion process in semi-continuous conditions was conducted in two bioreactors with a working volume of 3 dm^3. The bioreactors were operated at the following hydraulic retention times (HRT): 16, 18, 20, 22 and 24 days. The bioreactors were kept at a constant temperature of 36^{o}C and their content was mixed periodically – 5 min. in every 2–3 h. Bioreactors were maintained for at least three HRTs before decreasing of HRT value. The kit for measuring the amount of biogas generated included: calibrated cylinder filled with 5% NaCl solution and expansion tanks. The first reservoir allow reading of the amount of biogas produced. The volume of biogas produced was adjusted to standard temperature (0^{o}C) and pressure 1 · 10^5 Pa (1 atm) and expressed as daily methane production [dm^3/(dm^3 · day)] and methane yield [m^3/kg of VS_{added}].

Analytical methods

Total solids (TS), volatile solids (VS), ammonia (NH_4^+), total Kjeldahl nitrogen (TKN), total organic carbon (TOC), phosphates (PO_4^{3-}), total VFA and total alkalinity (TA) were determined in triplicate according to the standard methods [16]. The methane content in the biogas produced was determined using a gas analyzer Gas Data GFM 416.

Results and discussion

Anaerobic co-digestion in batch mode

The proper course of the fermentation process depends on a number of technological parameters, while, main objectives of the anaerobic processes, in controlled conditions, are focused on: intensification of organic matter mineralization and biogas production. Co-digestion of sewage sludge together with other organic wastes is one of the option

allowing to increase the efficiency of sludge anaerobic digestion [8]. The characteristics of the co-digestion mixtures before and after digestion is presented in Table 2.

Table 2

Characteristics of co-digestion mixtures before and after fermentation

Co-digested mixtures [%]	Before digestion			After digestion		
	pH [-]	VS [%]	C/N [-]	pH [-]	VS [%]	R_{VS} [%]
SAS (100%)	7.2	2.72 (0.14)	7.73	7.1	1.59 (0.06)	41.6 (1.0)
GF (1%) + SAS (99%)	7.2	3.46 (0.13)	18.5	7.1	1.74 (0.05)	50.0 (1.6)
GF (2%) + SAS (98%)	7.1	4.19 (0.13)	26.5	7.2	1.95 (0.10)	53.5 (1.0)
GF (3%) + SAS (97%)	7.1	4.93 (0.12)	32.7	7.2	2.19 (0.10)	55.5 (1.0)
GF (4%) + SAS (96%)	7.1	5.66 (0.12)	37.7	6.2	2.42 (0.11)	57.3 (1.1)
GF (5%) + SAS (95%)	7.0	6.40 (0.11)	41.7	6.1	2.55 (0.13)	60.2 (1.3)

* () – standard deviation; SAS – surplus activated sludge, GF – glycerine fraction, R_{VS} – organic matter removal.

Firstly, the influence of waste glycerol as a co-substrate on the organic matter removal was analysed. The digestion assay including the only sewage sludge exhibited the organic matter removal of 42%. Gradual increase of waste glycerine in the co-digested feedstock had a positive impact on the degree of organic matter removal. The degrees of organic matter removal amounted to 50–60% (Table 2), which can be attributed to the improvement of C/N ratio in the feedstock, – due to addition of co-substrate of high C/N ratio (Table 1), which also finds confirmation in previous reports [17, 18].

Secondly, the influence of glycerol addition as a co-substrate on the biogas production, was analysed. The average content of methane in the biogas produced was 57% (56–59%) and 66% (64–67%) in case of assays containing only sewage sludge and co-digestion mixtures, respectively (data not shown). Results presented as cumulative methane production are presented in Fig. 1. Even a small addition of waste glycerol (1%) to sewage sludge led to a significant increase of the total biogas production; *ie* 88%. A further increase in the proportion of glycerol in the feedstock undergoing fermentation led to a further increase of the amount of methane generated. The highest amount of methane produced (4.67 dm^3) was recorded for the mixture containing 3% of waste glycerol. The latter mixture allowed to receive more than a 4-fold increase of methane production in relation to the sample containing the sludge exclusively. The highest proportions of glycerol (4–5%) caused a significant decrease in methane production (Fig. 1). Fountoulakis et al [19] found that the most favorable proportion of glycerol in co-digestion mixtures, including primary and secondary sludge, amounted to

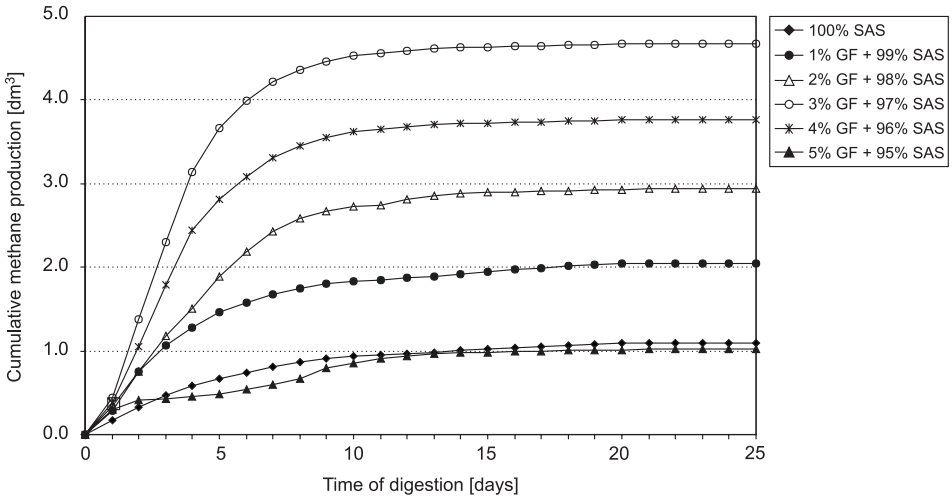

Fig. 1. The effect of glycerol addition to sewage sludge on the value of cumulative methane production

1% (by volume). This share has led to an increase in daily biogas production by over 100%.

Besides, glycerine fraction form biodiesel production, industrial waste with a high content of biodegradable components (*eg* wastes from meat processing or residues from fat separators) turned out to be an appropriate sewage sludge co-substrates [8, 20]. Wastes from this industry pose a threat to the environment, and their disposal is problematic for meat plants. According to research conducted by Lust and Luostarinen [21], the addition of 12.5–25.0% (by volume) of wastes from the meat industry (content and digestive systems, flotation sludge from wastewater treatment and fatty deposits) increased the methane production by 20%. Another study conducted by the same group of authors [22] revealed that the most preferred proportion of fatty wastes added to sewage sludge – amounted to 10% by volume, which was equivalent to 46% VS of the feedstock. In such conditions, more than 100% increase in daily and nearly 70% of the biogas yield were recorded. The addition of stillage (15% by volume) to sewage sludge also led to an 40% increase of biogas production.

Finally, the impact of feedstock enrichment on the anaerobic digestion stability was taken into account. Volatile fatty acids (VFA) accumulation leads to a significant decrease in pH value and thereby can inhibit the methanogenic phase of anaerobic digestion [23]. In the case of sewage sludge fermentation and co-digestion mixtures containing up to 3% of glycerol, there was no significant accumulation of VFA observed and the pH value was at a level ensuring proper course of anaerobic digestion (pH = 7.1–7.3) (Table 2 and 3). For mixtures including in its composition more than 3% of glycerol, concentrations of VFAs (3545–4248 mg/dm^3) and the ratio of VFA to alkalinity (0.92–1.31) increased above the value indicating the instability of the methanogenesis process (VFA > 2000 mg/dm^3; VFA/Alkalinity > 0.3–0.4) (Table 3) [8, 24, 25]. This was probably strictly connected with a decrease of pH value (6.1–6.2)

Table 3

Stability indicators of the batch co-digestion tests

Co-digested mixtures [%]	Indicator			
	VFA [mg/dm^3]	Alkalinity [mgCaCO$_3$/dm^3]	VFA/TA [-]	NH_4^+ [mg/dm^3]
SAS (100%)	429 (14)	4081 (24)	0.11	1420 (70)
GF (1%) + SAS (99%)	754 (14)	4610 (17)	0.16	1454 (85)
GF (2%) + SAS (98%)	909 (16)	4773 (67)	0.19	1398 (90)
GF (3%) + SAS (97%)	943 (10)	4825 (56)	0.20	1405 (85)
GF (4%) + SAS (96%)	3545 (110)	3853 (65)	0.92	1338 (90)
GF (5%) + SAS (95%)	4248 (220)	3233 (20)	1.31	1298 (82)

* () – standard deviation; SAS – surplus activated sludge, GF – glycerine fraction; VFA/TA – total volatile fatty acids to total alkalinity.

(Table 2). Although, ammonia released may counteract the decrease of pH values, excessive amounts of ammonia-nitrogen may also inhibit the methanogenic bacteria, and consequently lead to a decrease or even inhibit the production of biogas. The concentration of ammonia nitrogen greater than 3 g/dm^3 is generally considered as threshold value; above which the activity of methanogens is negatively affected [1, 8]. However, the concentration of ammonia-nitrogen in all analysed co-digestion mixtures did not exceed the above level (Table 3), thus the ammonia-nitrogen was not responsible for the deterioration of process stability of mixtures including more than 3% of glycerol. The stability indicators are presented in Table 3. Similar situation was observed in other studies. Increasing the excessive co-substrate content influenced the stability of the process in a negative way, *eg* stillage above 50% (by weight) resulted in VFA accumulation (4560–10 200 mg CH_3COOH/dm^3). A similar situation was observed after the addition of glycerol waste > 1% vol., which led to a high content of organic matter in post-digestion liquors and decrease of pH values (pH~5) due to accumulation of VFA [19].

Continuous anaerobic digestion of waste glycerine and sewage sludge

In this study, the mixture providing the highest effectiveness in batch co-digestion tests (3% of glycerine fraction + 97% of sludge) and an appropriate stability of the process was tested in continuous conditions. The sewage sludge was additionally treated with microwave irradiation with the aim to enhance the effectiveness of the overall co-digestion process; under the conditions determined during our previous studies [13, 14].

For all analysed co-digestion mixtures of sewage sludge (untreated) and glycerine fraction, reducing redox potential was obtained. These mixtures, with the exception of the shortest of HRTs (16–18 days), were characterized by the values of ORP in a range between –370 mV to –446 mV. The ORP values (–155 mV to –170 mV) recorded for

the HRT in range 16–18 days, were above values considered to be favorable for methane fermentation process (–300 mV) (Table 4) [26]. Mixtures including pretreated sludge instead of untreated sludge exhibited the ORP value between – 366 do – 435 mV (Table 4); which is in the favorable range for anaerobic digestion. Similarly to the results of ORP, the mixture containing untreated (microwaves) sludge exhibited some disturbance of pH values when digested for the HRT in the range of 16–18 days. The values indicated a significant decrease in pH value (pH 6.2–6.4), which was accompanied by increased concentrations of VFAs (4053–5445 mg CH_3COOH/dm^3) (Table 4). For all others retention times tested, pH values fluctuated between 7.1–7.6; *ie* the range most commonly reported for the proper course of anaerobic digestion, *eg* [8, 27].

Table 4

Characteristics of digested mixtures (glycerol + untreated sludge/pretreated sludge) related to different values of HRTs

Parameter	Co-digestion mixture 97% SAS + 3% GF					Co-digestion mixture 97% SASMD + 3% GF				
	HRT [day]									
	16	18	20	22	24	16	18	20	22	24
pH [-]	6.2 (0.1)*	6.4 (0.1)	7.3 (0.2)	7.4 (0.2)	7.5 (0.1)	7.1 (0.1)	7.3 (0.2)	7.5 (0.2)	7.6 (0.1)	7.6 (0.1)
ORP [mV]	–155 (41)	–170 (31)	–420 (25)	–446 (30)	–440 (20)	–366 (30)	–430 (20)	–425 (15)	–426 (20)	–433 (25)
VS [%]	25.8 (1.3)	22.7 (1.1)	20.4 (0.5)	19.7 (1.1)	19.5 (1.1)	22.2 (1.5)	19.1 (0.7)	18.0 (1.2)	18.4 (1.2)	18.7 (0.9)
VFA [mg/dm^3]	5445 (256)	4053 (285)	1225 (65)	1155 (55)	1090 (59)	2555 (166)	2256 (60)	1230 (52)	1180 (52)	1185 (55)
Alkalinity [$mg\ CaCO_3/dm^3$]	5855 (350)	6235 (280)	6419 (310)	6554 (225)	6550 (360)	6255 (250)	6565 (260)	6690 (305)	6960 (315)	7015 (240)

* () – standard deviation, SAS – surplus activated sludge without pre-treatment, SASMD – SAS after microwave disintegration, GF – glycerine fraction.

Organic matter removal

The most favorable conditions of anaerobic co-digestion (untreated sludge + glycerine fraction) were established. The highest values of organic matter removal (65–66%) were obtained for the HRT of 22–24 days, which corresponded with organic loading of the bioreactor at the level of 2.4–2.6 kg VS/($m^3 \cdot$ day). Figure 2 shows the effect of feedstock retention time in the bioreactor on the degree of organic matter removal. Mixtures containing the same amount of sludge, which was not subjected to the action of microwaves and digested for less than 20 days, resulted in a significant decrease in organic matter removal (56–60%). Under these conditions, a significant increase of the dissolved organic compounds has been observed (COD = 3845–9345 mg O_2/dm^3; data not shown). Modification of co-digestion mixtures by introducing pre-treated sludge caused only a slight increase of the organic matter removal, *ie* 67–69% (Fig. 2).

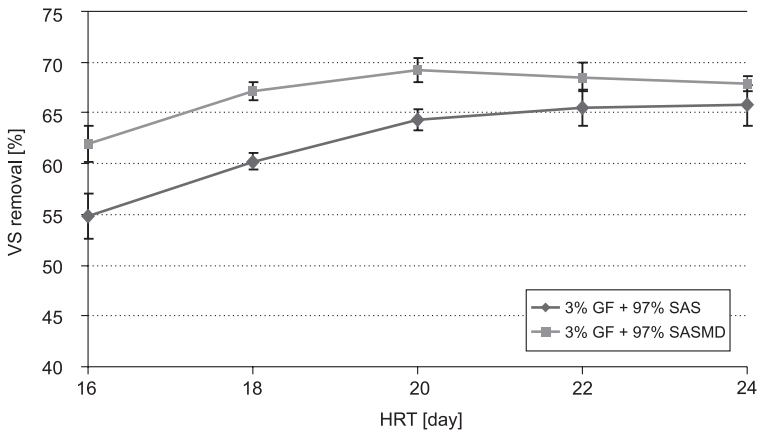

Fig. 2. Impact of HRTs and pre-treatment of feedstock (sewage sludge as a co-substrate) on degree of organic matter removal (SAS – surplus activated sludge without pre-treatment, SASMD – SAS after microwave disintegration, GF – glycerine fraction)

However, it is worth noting that the pre-treatment disintegration of the sludge being a part of co-digestion feedstock enabled to achieve these degrees of organic matter removal (67%) for much shorter retention times, *ie* 18 days. The latter value corresponds with the organic loading of the bioreactor at the level of 3.23 kg VS/(m^3 · day).

Biogas production

Secondly, the impact of different values of HRTs on the biogas production was taken into account. The amount of methane produced expressed as its daily methane production and methane yield are presented in Fig. 3 and 4 respectively. The highest values achieved during co-digestion of mixtures including untreated sludge amounting to 2.24 m^3/(m^3 · day) (methane production) and 0.29 m^3/kg VS (methane yield) were recorded for the HRT of 22 days. Further increase in HRT values led to a decrease of methane production indices. Decreasing the HRT value to 18–20 days also allowed to generate lower methane volumes, *ie* 1.51–1.76 (m^3/(m^3 · day)) and 0.16–0.21 m^3/kg VS. Whilst, during the process conducted for the lowest HRT, *ie* 16 days; a clear inhibition of the biogas (methane) production was noticed (0.96 m^3/(m^3 · day); 0.09 m^3/kg VS (Fig. 3 and 4); and these values are in the range obtained during the fermentation of sludge without the addition of a co-substrate reported previously [13]. This inhibition was probably caused by the accumulation of VFA (> 5445 mg CH_3COOH/dm^3) and higher organic matter loading of bioreactor's chamber, *ie* 3.57 kg VS/(m^3 · day) (Table 4).

Implementing the sludge pre-treated by microwaves influenced positively the methane production process. The highest values of methane production were recorded for the HRT of 18–22 days and amounted to about 2.60–2.70 m^3/(m^3 · day) (methane production) and 0.28–0.33 m^3/kg VS (methane yield) (Fig. 3 and 4). These values

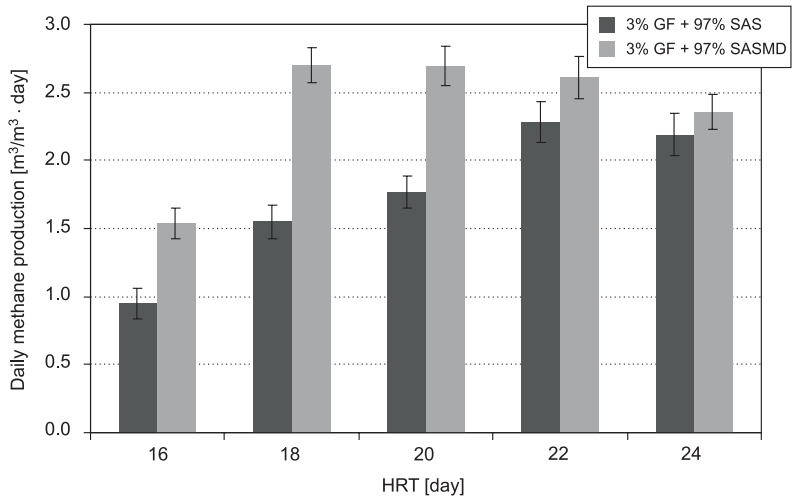

Fig. 3. Influence of hydraulic retention time of feedstock (glycerine fraction + untreated sludge; glycerine fraction + pretreated sludge) on daily methane production (SAS – surplus activated sludge, SASMD – SAS after microwave disintegration, GF – glycerine fraction)

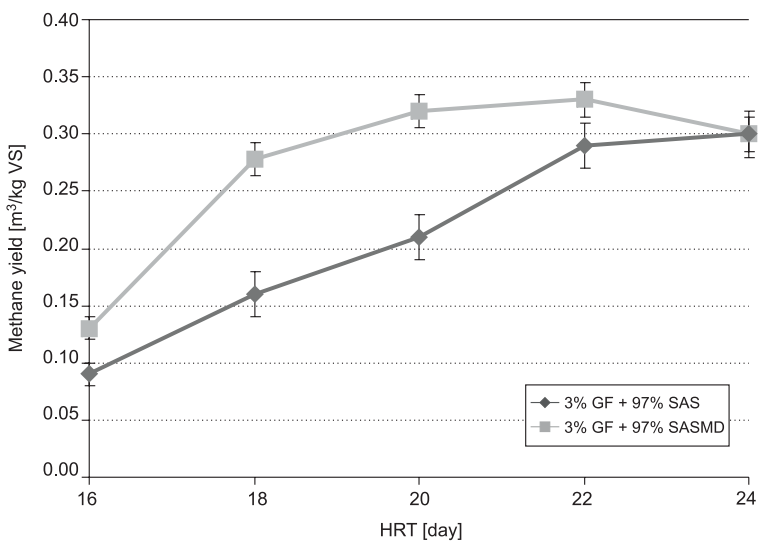

Fig. 4. Influence of hydraulic retention time of feedstock (glycerine fraction + untreated sludge; glycerine fraction + pretreated sludge) on methane yields (SAS – surplus activated sludge, SASMD – SAS after microwave disintegration, GF – glycerine fraction)

represent 52–74% (HRT = 18–20 days) and 14–15% (HRT = 22 days) increase of methane indices related to equivalent values obtained for mixture without pre-treated sludge. It is also worth mentioning that sludge pre-treatment allowed to achieve a high

methane production for shorter values of HRTs; compared to co-digestion mixtures containing the sludge without previous treatment.

Stability indicators of co-digestion

Finally, the influence of sludge microwave pretreatment on the stability of anaerobic digestion was taken into consideration. It was established that mixtures of glycerine and both types of sludge (untreated/pretreated) exhibited stable conditions for the HRT of > 18 days (VFA = 1090–1230 mg CH_3COOH/dm^3; VFA/Alkalinity = 0.16–0.19) (Table 4). These values of stability indices are in the range ensuring the stable course of the digestion processes [24, 25]. In case of lower HRTs values, a significant accumulation of VFA (2255–5445 mg CH_3COOH/dm^3) and increased the ratio of VFA/Alkalinity (0.41–0.93) were recorded. This is especially evident for the mixtures including glycerin fraction and sludge without pretreatment (Table 4).

Conclusions

The addition of glycerine fraction to sewage sludge turned out to be an effective way of increasing the mesophilic digestion of sewage sludge. Introducing sewage sludge after effective microwave disintegration into feedstock allowed to further improve the effectiveness of the co-digestion process analysed. The most favorable value of the biomass retention time (HRT) amounted 20 days; which allowed to achieve about 18–23% higher value of methane production and up to 10% higher methane yield compared to the values recorded in the conditions of the most appropriate digestion of glycerine and sludge without pre-treatment (HRT 22–24 days).

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KOFERMENTACJA MIESZANINY OSADÓW ŚCIEKOWYCH I FRAKCJI GLICERYNOWEJ WSPOMAGANA PROMIENIOWANIEM MIKROFALOWYM

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Abstrakt: Celem prowadzonych badań było opracowanie koncepcji zintegrowanego układu technologicznego, który zapewniłby wysoką efektywność kofermentacji produktów ubocznych pochodzących z wytwarzania biodiesla i osadów ściekowych. Dodatek frakcji glicerynowej do osadów ściekowych wpłynął korzystnie na stopień biodegradacji materii organicznej oraz na ilość i jakość wydzielanego biogazu. Zastosowanie jako

wsadu bioreaktora osadów ściekowych po dezintegracji mikrofalowej pozwoliło na dalszą poprawę efektywności analizowanego procesu kofermentacji. W odniesieniu do najkorzystniejszych warunków fermentacji mieszaniny osadów ściekowych nie poddawanych działaniu promieniowania mikrofalowego oraz frakcji glicerynowej (HRT = 22–24 dni) mieszanina kofermentacyjna zawierajaca w swym składzie osady po dezintegracji mikrofalowej (HRT = 20 dni) wygeneerowała 18–23% oraz do 10% więcej metanu w przeliczneiu odpowiednio na dobową oraz jednostkową produkcję metanu. Ponadto, zastosowanie wstępnej obróbki mikrofalowej pozwoliło na skrócenie czasu zatrzymania mieszaniny kofermentacyjnej w komorze bioreaktora o co najmniej 2 dni.

Słowa kluczowe: kofermentacja, frakcja glicerynowa, biodiesel, osady ściekowe, promieniowanie mikrofalowe

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SEEPAGE THROUGH MUNICPAL LANDFILL CLAY LINERS AFTER CYCLIC DRYING AND REWETTING

PRZESIĄK PRZEZ CYKLICZNIE OSUSZANE I NAWILŻANE PRZESŁONY MINERALNE SKŁADOWISK ODPADÓW KOMUNALNYCH

Abstract: The sustainability of municipal landfills and quality of water-soil environment is being compromised by the leachate percolation through the bottom sealing liner. The compacted mineral liners, using clays of various plasticity to assure the saturated hydraulic conductivity lower than $1 \cdot 10^{-9}$ m $\cdot$ s^{-1}, are among the most popular isolations of municipal waste landfills. But high plasticity clays present significant expansivity so they are prone to swelling, shrinkage and resultant cracking. Swelling and shrinkage of compacted clay liners, caused by cyclic drying and watering of substrate, are irreversible and after several cycles may result in a huge increase in the hydraulic conductivity and drastically reduced sealing capabilities of compacted clay liners. This paper presents the assessment of selected substrates' plasticity influence on the isolating capabilities of the municipal landfill's bottom liner undergoing cyclic drying and rewetting. The plasticity of tested clay materials was determined and classified by the standard methods. Saturated hydraulic conductivity of the studied clays formed by the standard Proctor method was measured by the laboratory falling head permeameters for compacted soils. Measurements of saturated hydraulic conductivity of the tested substrates after three cycles of drying and rewetting were performed in the standard 100 cm^3 steel cylinders by the falling and constant head laboratory permeameter. Shrinkage of the tested compacted specimens was determined also in the standard 100 cm^3 steel cylinders and classified basing on dimensionless indicator *COLE*. Determination of water seepage through the tested bottom compacted clay liners was based on the standard form of Darcy law for the saturated conditions of soil medium. The obtained results showed influence of plasticity of clays on decrease in their sealing capabilities after several cycles of drying and rewetting and, by extension, undesirable increase in the seepage volume through the compacted bottom liner.

Keywords: clay materials, compacted mineral liners, hydraulic conductivity, sustainable landfilling

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Introduction

The sustainable landfilling should be understood as "the safe disposal of waste within a landfill, and its subsequent degradation to the inert state in the shortest possible time-span, by the most financially efficient method available, and with minimal damage to the environment" [1]. The environmental impacts, related to limiting the possible threats to water and soil are the crucial issue among the all possible aspects of sustainable landfilling [2]. The most serious threats to water, including surface water and groundwater, as well as to soil are posed by leachate percolating through the liners isolating landfill from the environment [3–5]. Thus, leachate seepage from the deposited waste body should be completely prevented by the landfill's bottom liners, which are often constructed using the natural materials of appropriate permeability (commonly below $1 \cdot 10^{-9}$ m $\cdot$ s^{-1} [6–8]), frequently additionally supported by the plastic or geosynthetic membranes [9–13]. So, in the presented case, the sustainability of the landfill is going to be related to the sustainability and durability of its bottom liner.

Bottom landfills' liners are commonly based on various types of the compacted clays as the natural mineral materials presenting a very low hydraulic conductivity [14, 15]. But compacted clays, or even some sandy soils containing fine particles, present significant expansiveness, related, among the others, to their plasticity and forming conditions [16, 17]. The expansive clayey soils significantly increase their volume (swell) when saturated and when dewatered they reduce their volume (shrink) [16]. Swelling and shrinkage are the irreversible processes resulting in cracking and changes in unsaturated and saturated hydraulic conductivity; soils or substrates specimens once swelled or shrinked are generally unable to return to their initial characteristics [17]. The observed increase in hydraulic conductivity is generally related to forming conditions, the grater molding water content applied, the higher possible increment of hydraulic conductivity after shrinkage [15–18].

The each following cycle of drying and rewetting alters swelling and shrinkage properties as well as hydraulic characteristics of clays. The equilibrium was reported to be usually achieved after several cycles (3 to 5), when changes in expansivity of clays are already limited. But the resultant hydraulic conductivity of clays specimens after reaching equilibrium may increase significantly, even by several orders of magnitude, to the values typical for the coarse sandy soils [17–24]. The discussed decrease in sealing capabilities of compacted clay liners after several cycles of drying and wetting is also related to forming conditions, including initial water content [17, 18].

So in our opinion, the sustainability and durability of the compacted clay liners may be reduced by the decrease in their sealing capabilities caused by changes in their hydraulic properties related to molding conditions and soil properties, including forming water content and plasticity, as well as to changes caused by cyclic drying and rewetting.

This paper presents the attempt of determination the influence of the plasticity of the selected substrates for compacted clay liner of municipal landfill undergoing cyclic drying and rewetting on the isolating capabilities of the municipal landfill's bottom liner constructed according to the actual, biding standards.

Materials and methods

The presented studies were based on the clay materials sampled in six locations close to Lublin, SE part of Poland: Bychawa, Lazek Ordynacki, Pawlow, Mejznerzyn, Markowicze and Gawlowka [25]. Materials sampled in Bychawa and Lazek Ordynacki were recognized as silty clays, while in Pawlow and Mejznerzyn as clays. Finally, substrates from Markowicze and Gawlowka were described as clay loam and sandy clay loam, respectively. The basic characteristics of the sampled substrates are presented in Table 1.

Table 1

Basic characteristics of the tested clay materials, modified after Stepniewski et al [24] and Widomski [18]

Substrate		Bychawa	Lazek Ordynacki	Pawlow	Mejznerzyn	Markowicze	Gawlowka
Particle fraction	Sand [%]	12	4.5	11	13	25	66
	Silt [%]	46	51	37	35	37	3
	Clay [%]	42	44.5	52	52	38	31
Solid particle density [$Mg \cdot m^{-3}$]		2.72	2.68	2.61	2.79	2.76	2.86
Bulk density [$Mg \cdot m^{-3}$]		1.64	1.70	1.67	1.37	1.97	1.95
Saturated hydraulic conductivity in situ [$m \cdot s^{-1}$]		$2.75 \cdot 10^{-10}$	$1.37 \cdot 10^{-10}$	$2.51 \cdot 10^{-10}$	$2.05 \cdot 10^{-10}$	$1.00 \cdot 10^{-10}$	$4.73 \cdot 10^{-10}$

The particle size distribution of the tested clayey materials was determined according to the Polish national standard PN-B-04481:1988 [26], while solid particle density was measured in le Chatelier flask and gravimetric water content was obtained by the standard weight method according to ASTM C566-13 [27]. The Atterberg limits, including liquid limit and plasticity index of tested clay materials were determined by the standardized methods [28] and classified according to the Unified Soil Classification System [29]. Saturated hydraulic conductivity (K_s) of the studied substrates under their natural conditions was measured in situ by the field falling head permeameter BAT for fine grained soils produced by GeoNordic, Sweden.

Laboratory measurements of saturated conductivity of the tested substrates after forming at different initial water contents were performed in the permeameters for compacted soil specimens by Humboldt Mfg. Co, USA. The falling water head H-4145 compaction permeameters, meeting requirements of ASTM D5856-95 [30], were applied to our studies. The tested clay substrates were compacted, according to PN-B-04481:1988 [26] at the optimum water content (w_{opt}) and at commonly advised for compacted liner construction 95% of maximum bulk density, wet of optimum $w_{opt} < w_f < 1.2\ w_{opt}$ and dry of optimum, at $w_f < w_{opt}$.

The applied H-4145 were supplied with water from the top, according to the scheme presented in Fig. 1, after [18].

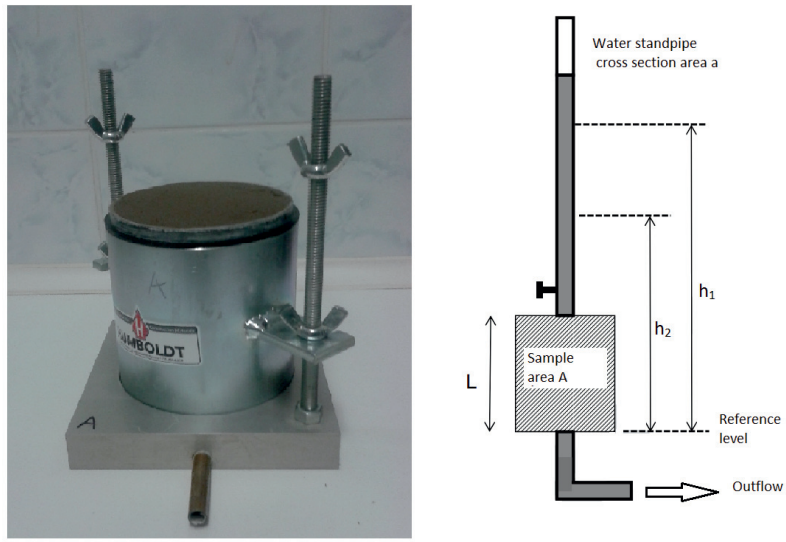

Fig. 1. Laboratory permeameter for compacted specimens H-4145 and scheme of its application, after [18]

Saturated hydraulic conductivity of compacted specimens of tested clayey materials was determined by the falling head method and the standard formula presented below, after *eg* [18]:

$$K_s = \frac{a \cdot L}{A_s \cdot \Delta t} \ln \frac{h_1}{h_2}$$

where: K_s – coefficient of saturated hydraulic conductivity, [m · s^{-1}];
a – water standpipe cross section area, [m^2];
A_s – soil sample cross section area, [m^2];
L – soil sample height, [m];
h_1, h_2 – water level heights, [m];
Δt – time duration required for lowering water level from h_1 to h_2, [s].

Measurements of saturated hydraulic conductivity in H-4145 rigid wall permeameters were continued until observation of constant values of the resultant K_s.

The saturated hydraulic conductivity of the tested materials after three cycles of shrinkage and swelling, was determined for compacted and saturated specimens sampled to the standard 100 cm^3 steel cylinders directly from the compaction molds. All the samples were first air dried at room temperature, approx. 20^{o}C degree, and afterwards slowly rewetted by the capillary saturation. After each applied drying and wetting cycle, saturated hydraulic conductivity was measured by the constant or falling head method, (depending on the value of the measured parameter, above $K_s = 1 \cdot 10^{-5}$ m · s^{-1} the constant head method was used) in the laboratory permeameter, produced by the former IMUZ, Lublin, Poland.

Shrinkage of clays compacted wet and dry of optimum for approx. 95% of optimum density was measured in 100 cm^3 steel cylinders, sampled directly from the compaction molds, according to the methodology similar to that reported by Peng et al [31], Dorner et al [21] and Gerbhardt et al [32]. Shrinkage of the cylindrical samples was measured by a vernier caliper with the accuracy of 0.05 mm in 8 selected locations (as repetitions), both for the diameter and the height. Afterwards, the measured dimensions were used to calculate dimensionless shrinkage indicator, coefficient of linear extensibility *COLE* [33, 34], according to the following formula:

$$COLE = \left(\frac{V_s}{V_d} \right)^{\frac{1}{3}} - 1$$

where: *COLE* – dimensionless coefficient of linear extensibility;
V_d – dry specimen volume, [m^3];
V_s – saturated specimen volume, [m^3].

The values of the coefficient of linear extensibility (*COLE*) indicate the shrinkage potential according the ranges [32]: i) < 0.03 a low shrinkage potential; ii) 0.03–0.06 a moderate shrinkage potential; iii) 0.06 to 0.09 a high potential; iv) > 0.09 a very high shrinkage potential.

Assessment of seepage through the bottom liners utilizing the tested clayey substrates determined for the assumption of its operation at saturated, or very close to saturated, conditions. Thus, the standard form of Darcy equation was used for determination of the seepage flux for 1 m^2 of liner area:

$$q_D = K_s \frac{dh}{dl}$$

where: q_D – Darcy unit flux, [$m \cdot s^{-1}$];
dh/dl – pressure head gradient.

Calculations of seepage were performed in MS Excel, for the assumed thickness of bottom compacted clay liner equal to 1 m, meeting the requirements of the Polish national standards [7], and constant pressure head 0.3 m, as typical maximum leachate head over the bottom liner for the normally operating municipal landfill [35]. The assessment was performed for K_s measured in the laboratory conditions for substrates formed at 95% of maximum bulk density and two molding water contents $w_{opt} < w_f < 1.2\ w_{opt}$ and $w_f < w_{opt}$.

Results and discussion

The results of tested clay substrates plasticity determination, supported by the basic determination of swelling and shrinkage potentials as well as the measured saturated hydraulic conductivity K_s for the optimal water content w_{opt} and the applied molding water w_f content are presented on plasticity chart in Fig. 2 and in Table 2.

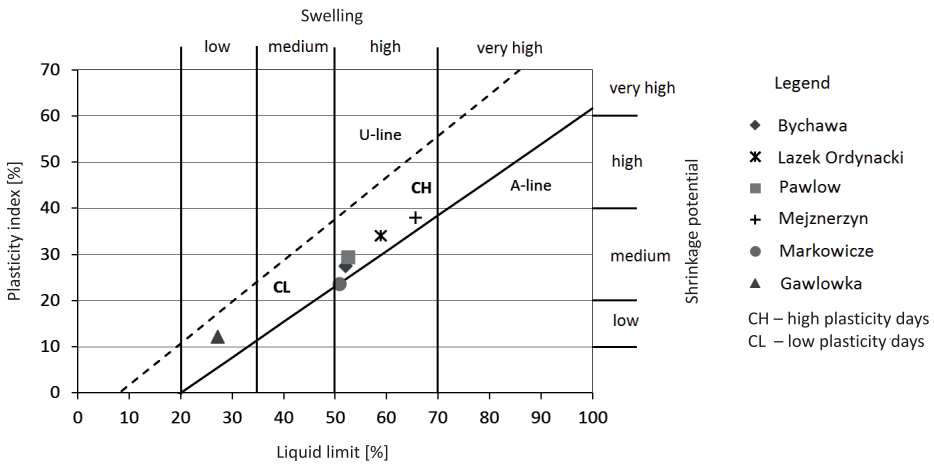

Fig. 2. Plasticity chart of tested clay substrates, modified after [25]

Table 2

Compaction results for tested substrates formed also wet and dry of optimum

Substrate	Bychawa	Lazek Ordynacki	Pawlow	Mejznerzyn	Markowicze	Gawlowka
Maximum density						
w_{opt} [kg · kg^{-1}]	0.22	0.21	0.19	0.26	0.16	0.13
Bulk density [kg · m^{-3}]	1.71	1.72	1.78	1.56	1.83	1.99
K_s at w_{opt} [m · s^{-1}]	$2.75 \cdot 10^{-11}$	$2.09 \cdot 10^{-11}$	$5.66 \cdot 10^{-11}$	$2.86 \cdot 10^{-11}$	$9.35 \cdot 10^{-11}$	$4.42 \cdot 10^{-10}$
Molding wet of optimum						
w_f for $w_{opt} < w_f < 1.2\ w_{opt}$ [kg · kg^{-1}]	0.25	0.25	0.22	0.30	0.20	0.15
Bulk density [kg · m^{-3}]	1.60	1.62	1.68	1.52	1.74	1.90
K_s at $w_{opt} < w_f < 1.2\ w_{opt}$ [m · s^{-1}]	$6.15 \cdot 10^{-11}$	$5.20 \cdot 10^{-11}$	$4.17 \cdot 10^{-11}$	$2.46 \cdot 10^{-11}$	$1.17 \cdot 10^{-10}$	$9.45 \cdot 10^{-11}$
Molding dry of optimum						
w_f for $w_f < w_{opt}$ [kg · kg^{-1}]	0.20	0.19	0.16	0.2	0.15	0.08
Bulk density [kg · m^{-3}]	1.67	1.69	1.69	1.49	1.79	1.89
K_s at $w_f < w_{opt}$ [m · s^{-1}]	$1.11 \cdot 10^{-10}$	$8.43 \cdot 10^{-11}$	$4.43 \cdot 10^{-11}$	$2.20 \cdot 10^{-10}$	$8.80 \cdot 10^{-10}$	$4.40 \cdot 10^{-10}$
Recognized type of clay	CH	CH	CH	CH	CH	CL

The results presented in Fig. 2 and Table 2 show that all the tested clay substrates, regarding their different particle composition and Atterberg limits allowed the required value of saturated hydraulic conductivity lower than $1 \cdot 10^{-9}$ m · s^{-1} for optimum and forming water contents, wet and dry of optimum, for approx. 95% of maximal density in ranges of $w_{opt} < w_f < 1.2\ w_{opt}$ and $w_f < w_{opt}$. However, in case of substrates sampled in

Pawlow and Markowicze, it was not possible to obtain $K_s < 1 \cdot 10^{-9}$ m · s^{-1} for precise 95% of optimum density when specimens were compacted at low initial water contents dry of optimum, thus in this case the grater forming water content was applied. It is also visible that most of the tested clay substrates were recognized as high-plasticity clays according to USCS [29]. The only noted exception was Gawlowka sandy clay loam recognized as low plasticity clay.

Figure 3 shows results of measurements of K_s after three subsequent cycles of drying and rewetting, resulting in cyclic shrinkage and swelling.

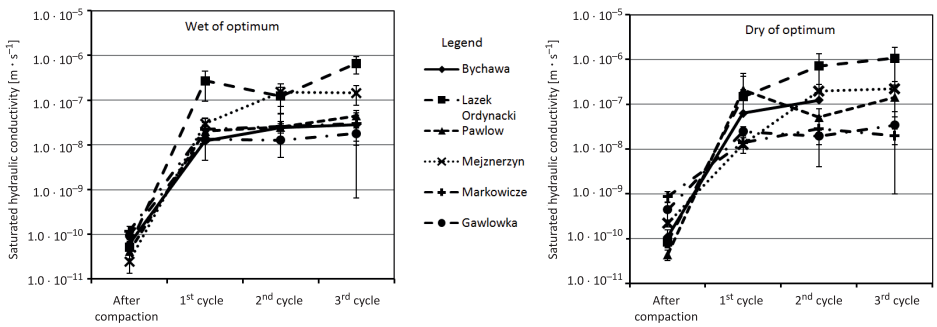

Fig. 3. Measured K_s after subsequent cycles of drying-rewetting for substrates formed wet dry of optimum

The results of K_s measurements presented in Fig. 3 show that none of the tested substrates, compacted both, wet and dry of optimum, was able to sustain its sealing capabilities after three cycles of drying and rewetting. In all the tested cases the measured saturated hydraulic conductivity after the subsequent cycles of shrinkage and swelling was greater than commonly allowed $1 \cdot 10^{-9}$ m · s^{-1}. The greatest changes of saturated hydraulic conductivity were observed for the first cycle of drying and rewetting when measured K_s increased by several orders of magnitude, from the range of 10^{-11}–10^{-10} m · s^{-1} to the values between 10^{-8} and 10^{-7} m · s^{-1}. The highest increase for compaction wet of optimum after the first drying and rewetting was noted for Lazek Ordynacki clay substrate, the resultant K_s exceeded the level of 10^{-7} m · s^{-1}. Additionally, for tested specimens formed dry of optimum, the most significant increased values of hydraulic conductivity were noted for samples from Lazek Ordynacki and Pawlow. In all of the mentioned cases the high-plasticity clays were considered.

Similarly, the greatest total increase in K_s values was observed for substrates of the highest plasticity indices, compacted dry and wet of optimum, *ie* Lazek Ordynacki and Mejznerzyn, for which the K_s after the 3rd cycle exceeded even the value of $1 \cdot 10^{-7}$ m · s^{-1} allowed by the American standards for the top cover of municipal landfill [35]. Additionally, we may state that compaction dry of optimum in most cases resulted in higher saturated hydraulic conductivity after forming (as it was presented in Table 2) and after cyclic drying and rewetting. The lowest values of increased K_s were observed for substrates sampled in Markowicze and Gawlowka, containing significant sand

content. The measured K_s for these clayey materials after the third cycle of drying and rewetting reached the level between approx. $1.8 \cdot 10^{-8}$ m $\cdot$ s^{-1} and $3.4 \cdot 10^{-8}$ m $\cdot$ s^{-1}, both, for compaction wet and dry of optimum.

The observed relation between determined indices of plasticity and resultant K_s after the final third cycle of drying and rewetting for the tested substrates compacted wet and dry of optimum is presented in Fig. 4.

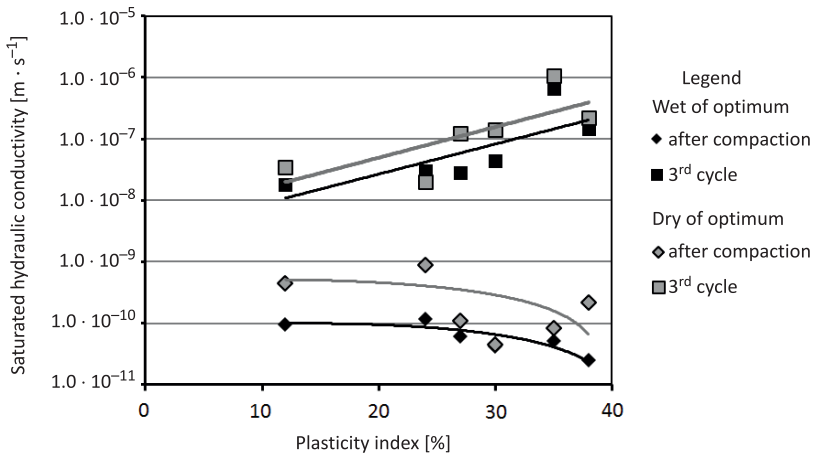

Fig. 4. Relation between plasticity and K_s of clays after compaction and after the final cycle of shrinkage and swelling

It is clearly visible in Fig. 4 that the increase in plasticity index of compacted substrate allows to achieve the greater decrease of its saturated hydraulic conductivity after forming, resulting in better sealing capabilities of the compacted clay liner. In both applied cases of the initial forming water content, wet and dry of the optimum, the obtained resultant K_s values were similar but it should be noted that K_s for specimens of the same plasticity were lower when substrates were formed wet of optimum. But, on the other hand, the higher plasticity led to increased cracking and decrease in substrates' sealing capability by increase in hydraulic conductivity. And again, the general tendency of the measured saturated hydraulic conductivity for specimens formed wet of optimum presented slightly lower values then than for the specimens of the same plasticity index but compacted dry of optimum.

The performed studies covered also assessment of shrinkage potential in regard to the plasticity of compacted substrate and forming conditions. The results of dimensionless *COLE* determination for substrates formed wet and dry of optimum are presented in Fig. 5.

Figure 5 shows some very important issues concerning influence of plasticity of clayey soils for the different substrates compacted at applied moisture contents wet and dry of optimum. It is clearly visible that plasticity of clayey materials affects its shrinkage properties. The grater plasticity index, the higher value of *COLE* determined, thus the higher shrinkage potential. The greatest values of *COLE*, exceeding 0.10, typical for the very high shrinkage potential were observed for substrate sampled in

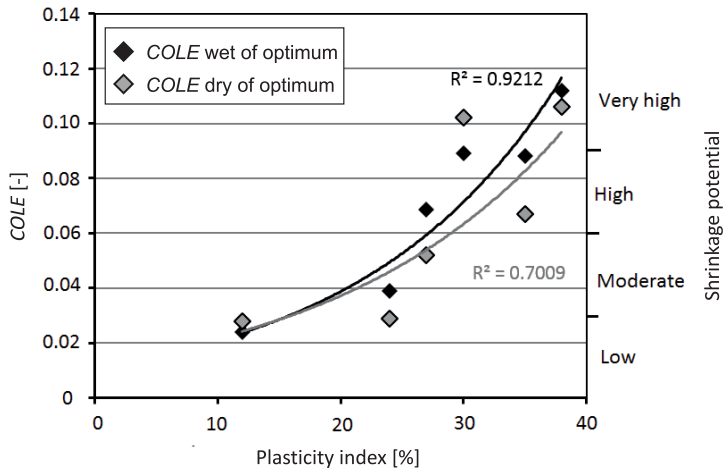

Fig. 5. Assessment of shrinkage potential indicator *COLE* for tested substrates, compacted wet and dry of optimum

Mejznerzyn of the highest plasticity index, equal to 38%. Most of the studied substrates, including Bychawa, Lazek Ordynacki and Pawlow specimens presented high shrinkage potential, while Markowicze clay showed moderate shrinkage potential. The lowest shrinkage was observed for Gawlowka sandy clay loam for which *COLE* indicated low shrinkage potential. Figure 5 shows also that conditions of forming considerably affect the resultant shrinkage, the determined *COLE* indicator for the same values of plasticity was greater for w_f wet of optimum.

To fully underline the above presented phenomena, daily seepage assessment was performed for 1 m^2 meter of the bottom liner constructed to meet the actual Polish and European landfilling standards [6–8] and utilizing tested substrates as the sealing material, compacted wet and dry of the optimum. The results of our calculations are presented in Fig. 6.

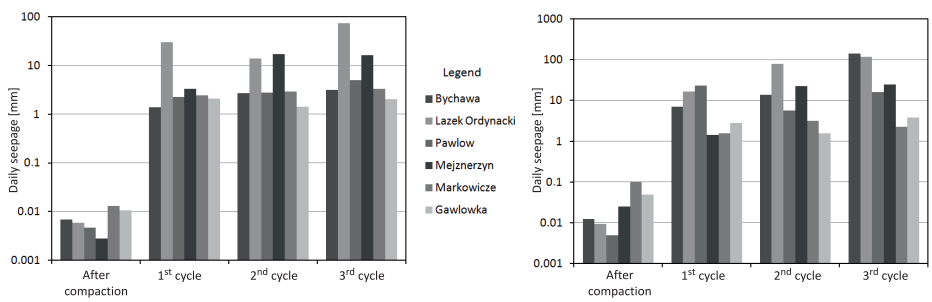

Fig. 6. Calculated daily seepage for each studied substrate and phase of cyclic drying and rewetting

As it is visible in Fig. 6, the irreversible changes in compacted clays structure caused by cyclic shrinkage and swelling resulted in clear increase in the calculated daily seepage for compaction on both sides of Proctor curve. The tested clay materials

directly after compaction wet of optimum showed satisfactory sealing capabilities allowing the daily seepage max. at the level of 0.01 mm. The same specimens compacted dry of optimum showed slightly greater seepage, but lover than 0.1 mm per day.

Then, cyclic drying and rewetting drastically reduced the sealing capabilities of the tested clay substrates, the calculated seepage increased by 2–3 orders of magnitude, for samples compacted both, wet and dry of optimum. Generally, the higher increase in seepage was observed for samples compacted dry of optimum. The calculated daily seepage for Bychawa and Lazek Ordynacki after the final cycle of drying and rewetting reached the very high level of 143 and 119 mm, respectively.

The greatest increase in calculated seepage values for substrates compacted wet of optimum were observed for substrates of the highest noted plasticity indices, *ie* materials sampled in Lazek Ordynacki and Mejznerzyn. The observed values of daily seepage reached the level of 16 and 74 mm after the third, final tested cycle of shrinkage and swelling for Lazek Ordynacki and Mejznerzyn substrates, respectively.

Additionally, it is worth to note, that for both tested molding water contents, wet and dry of optimum, the lowest daily seepage from range 2–4 mm per day, were observed for substrates of low plasticity, low clay and significant sand fraction content, *ie* Markowicze and Gawlowka specimens.

Summary and conclusions

Our studies showed that despite the fact that all the tested clayey substrates were able to assure the required significant sealing capabilities due to a very low value of K_s after compaction, the cyclic shrinkage and swelling drastically reduced the sealing capabilities of the tested materials. The irreversible cracking of the studied substrates triggered the significant increase in their saturated hydraulic conductivity, thus, leading to the enhanced volume of daily seepage. However, the observed increase in seepage was not uniform. There was observed the relation between the plasticity index of clays and increase in K_s and resultant seepage after cyclic drying and rewetting. Generally, the higher plasticity index of tested substrate, the greater K_s and resultant seepage after shrinkage and swelling were observed. Thus, in our opinion, the high plasticity clays presenting a significant decrease in their sealing capabilities after several cycles of drying and rewetting should be avoided in construction of compacted clay liners to ensure the long-term sustainability of landfill isolation and prevent increased pollutants migration to the natural soil and water environment.

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PRZESIĄK PRZEZ CYKLICZNIE OSUSZANE I NAWILŻANE PRZESŁONY MINERALNE SKŁADOWISK ODPADÓW KOMUNALNYCH

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Abstrakt: Zrównoważoność składowisk odpadów komunalnych oraz jakość środowiska gruntowo-wodnego mogą być zagrożone przez infiltrację odcieków poprzez dno składowiska. Zagęszczone przesłony mineralne, wykonane z materiałów ilastych o różnej plastyczności, zapewniające współczynnik filtracji warstwy niższy niż $1 \cdot 10^{-9}$ m $\cdot$ s^{-1}, są jednym z podstawowych sposobów zapewniania izolacji składowisk. Jednak grunty ilaste o wysokiej plastyczności są materiałami ekspansywnymi, podatnymi na pęcznienie, skurcz oraz spękanie. Pęcznienie i skurcz zagęszczonych gruntów ilastych wywołane przez kolejne, następujące po sobie cykle nawilżania i osuszania zagęszczonej ilastej przesłony mineralnej są nieodwracalne i po kilku cyklach mogą doprowadzić do znacznego zwiększenia przewodnictwa wodnego, jednocześnie drastycznie zmniejszając zdolności izolacyjne zagęszczonych iłów. Praca niniejsza przedstawia próbę oceny wpływu plastyczności wybranych gruntów ilastych na właściwości izolacyjne przesłony składowiska poddanej cyklicznemu osuszaniu i nawilżaniu.

Plastyczność badanych gruntów określono metodami standardowymi i sklasyfikowano według Unified Soil Classification System. Współczynnik filtracji gruntów po zagęszczeniu wyznaczono za pomocą laboratoryjnych przepuszczalnościomierzy do gruntów zagęszczonych. Pomiary współczynnika filtracji dla próbek w cylindrach 100 cm^3 po trzech cyklach osuszania i nawilżania przeprowadzono za pomocą przepuszczalnościomierza laboratoryjnego. Skurcz badanych próbek zagęszczonego gruntu pomierzono także w cylindrach 100 cm^3 i sklasyfikowano z użyciem wskaźnika *COLE*. Obliczenia przesiąku przez dolną zagęszczoną warstwę izolacyjną składowiska oparto o standardową postać równania Darcy dla strefy saturacji. Uzyskane wyniki wykazały wpływ plastyczności iłów na zmniejszenie ich właściwości izolacyjnych po kolejnych cyklach osuszania i nawilżania, a co za tym idzie niepożądany wzrost objętości przesiąku przez dolną warstwę izolacyjną składowiska.

Słowa kluczowe: materiały ilaste, zagęszczone przesłony mineralne, przewodnictwo hydrauliczne, zrównoważone składowiska odpadów

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THE INFLUENCE OF EFFECTIVE MICROORGANISMS APPLICATION ON THE CHEMICAL COMPOSITION IN LETTUCE GROWN UNDER COVER

WPŁYW ZASTOSOWANIA EFEKTYWNYCH MIKROORGANIZMÓW NA SKŁAD CHEMICZNY SAŁATY UPRAWIANEJ POD OSŁONAMI

Abstract: The aim of the study was to assess the influence of Effective Microorganisms (EM) on the content of nutrients in the leaves of lettuce (*Lactuca sativa* L. 'Sunny') grown under cover in the spring-summer season and in autumn. The influence of the following methods of EM application was assessed: root treatment, leaf treatment and seed inoculation. When EM was applied into the roots, plants were irrigated with a 1% solution of the EM-A preparation or with EM-5 (250 cm^3 of the liquid per plant), depending on the combination. The same preparations concentrated at 1% were sprayed on the leaves. Seeds were inoculated immediately before being sown (they were soaked for 30 minutes in a 10% solution of the EM-A preparation). During the growing season the plants were sprayed or irrigated four times at three-day intervals. Effective Microorganisms was not used in the control combination. The research proved the influence of EM on the content of nutrients in lettuce leaves. When the plants were irrigated and sprayed with EM-5, they had higher content of nitrogen. They were significantly better nourished with phosphorus, when the seeds were inoculated with EM-A, when the plants were sprayed with EM-5 at both terms of cultivation and when the plants were irrigated with EM-A in autumn. In comparison with the control combination the application of EM preparations significantly increased the content of potassium in the lettuce leaves. Simultaneously, the content of potassium generally tended to increase significantly when the plants were irrigated with both preparations and sprayed with EM-5 in the spring-summer season. The highest content of magnesium was noted when the plants were irrigated with EM. The inoculation of seeds resulted in the lowest content of this element. The tendencies were similar at both terms of cultivation. As far as the content of microelements is concerned, the application of EM at both terms of cultivation resulted in a significant increasing tendency in

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the content of iron and zinc in the lettuce leaves. The volume of increase depended on the method of application of the preparations.

Keywords: Effective Microorganism (EM), lettuce, nutrients, microelements, macroelements

Introduction

In recent years there has been growing interest in the possibility to apply biopreparations based on Effective Microorganisms (EM) for agricultural and horticultural production. These biopreparations were invented in Japan by Professor Terou Higa [1]. They contain coexisting species of different useful microorganisms and they are increasingly often recommended for organic cultivation. Many scientific centres all over the world are testing the effectiveness of these preparations. Researchers have found that the use of Effective Microorganisms may help to restore the lumpy structure of soil [2], increase the assimilability of macro- and microelements to plants [3], accelerate organic matter humification [4] and limit the process of decay [5]. In many cases the application of Effective Microorganisms increased the count of other useful microorganisms in soil [6]. EM may induce the photosynthetic process, increase plants' natural resistance to stress factors and neutralise the effects of drought [7]. Useful microorganisms can inhibit the development of different pathogenic factors, especially those developing in plants' roots, by releasing different substances, which are toxic to pathogens [8]. The application of Effective Microorganisms to seeds and planting material may accelerate seed germination [9, 10] and improve the development of roots [11]. Effective Microorganisms may positively influence the growth of plants and their florescence [12–14] and increase the yield, as was observed in studies on agricultural crops (peas, maize, wheat, potato) [3, 15–19] and horticultural plants (onion, apple-tree, tomato, saffron) [3, 7, 12, 20]. Better yield quality was also observed [7].

However, as results from studies conducted so far, the effects are not always replicable and they depend on numerous factors, such as the quality of the preparation with Effective Microorganisms, its form and frequency of use [21]. There are also reports on the ineffectiveness of Effective Microorganisms in plant cultivation [21–24].

Biopreparations with Effective Microorganisms may be applied in different ways, *eg* by inoculation of the substrate prepared for cultivation, soil irrigation and spraying. It is also possible to apply them directly to plants by spraying or seed inoculation.

The aim of the study was to assess the influence of different methods of application of Effective Microorganisms (EM) on the content of nutrients in the leaves of lettuce grown under cover.

Material and methods

The research on the influence of Effective Microorganisms (EM) on the content of nutrients (macro- and microelements) and sodium in butterhead lettuce leaves (*Lactuca sativa* 'Sunny') was conducted in 2013 (two independent cultivation cycles in the spring-summer season – May-June and in autumn – October) at the Experimental Station of Departments of the Faculty of Horticulture and Landscape Architecture,

Poznan University of Life Sciences. The experiment was conducted in an unheated polytunnel, in a systemic arrangement with ten replicates. During the entire growing season we applied agrotechnical procedures according to current recommendations.

The following methods of EM application were researched: root treatment (1), leaf treatment (2) and seed inoculation (3). The plants which were not treated with EM were used as the control combination. When EM was applied into the roots, plants were irrigated with a 1% solution of the EM-A preparation (Naturally Active EM) or with EM-5 (250 cm^3 of the liquid per plant), depending on the combination. The same preparations concentrated at 1% were sprayed on the leaves. They were applied with a hand-held sprayer 'Orion' equipped with a slot nozzle TeeJet XR 11003 at a constant pressure of 3 atm (conversion dose: 300 dm^3 of working liquid per ha). Seeds were soaked for 30 minutes in a 10% solution of the EM-A preparation immediately before being sown.

During the growing season the plants were sprayed or irrigated four times (in corresponding combinations) at three-day intervals. The preparations were applied on 24 May, 27 May, 30 May and 2 June 2013 in the spring-summer season and on 1 October, 4 October, 8 October and 11 October 2013 in the autumn cycle.

The plants grew in 5 dm^3 pots filled with peat substrate of the following chemical composition (mg · dm^{-3}): N 150, P 150, K 175, Mg 150, pH 6.50. The plants were watered when necessary to maintain constant humidity of the substrate.

On the last day of each growing cycle the aerial parts of the plants were collected for chemical analyses. The collected material was dried at 45–50^oC and ground. In order to assay the total forms of nitrogen, phosphorus, potassium, calcium, magnesium and sodium, the plant material (1 g) was digested in concentrated (96%, pure per analysis) sulphuric acid (20 cm^3) with the addition of 60 cm^3 of hydrogen peroxide (30%, pure per analysis). For analyses of total iron, manganese, zinc and copper the plant material (2.5 g) was digested in a 30 cm^3 mixture of concentrated nitric (ultra-pure) and perchloric acids (analytically pure) at a 3:1 ratio. After mineralisation of the plant material the following measurements were made: N-total – using the distillation method according to Kjeldahl in a Parnas Wagner apparatus; P – colorimetric analysis with ammonium molybdate; and K, Ca, Mg, Fe, Mn, Zn and Cu – using flame atomic absorption (on an AAS, Carl Zeiss Jena apparatus). The results of the chemical analyses were analysed statistically by means of Duncan's test, at a significance level $\alpha = 0.05$.

Results and discussion

Macroelements and sodium. Both cultivation cycles proved the multidirectional effect of EM on the content of nitrogen in the plants. It improved in the EM-5 combination (both after irrigation and spraying). However, there were no significant differences between the EM-A combination and the control variant (Tables 1 and 2). There was a significantly higher content of phosphorus in the plants when the seeds were inoculated with the EM-A preparation and when the plants were sprayed with the EM-5 in the spring-summer season. The same tendencies were observed in the autumn cycle, but there was significant improvement when the plants were irrigated with the

EM-A. The application of the EM preparations significantly increased the content of potassium in lettuce leaves (as compared with the control combination) and there was also a general increasing tendency for the content of calcium (it was significant after irrigation with both preparations and after spraying the EM-5 in the spring-summer season). There were significant differences in the content of magnesium between the combinations. The highest content was noted when the plants were irrigated with EM, the lowest – after seed inoculation (there were similar tendencies at both terms). The analyses proved significant differences in the content of sodium in lettuce leaves. The smallest content of this ballast ion was noted after irrigation with the EM-A preparation. It was higher in the other combinations.

Table 1

The influence of EM on the chemical composition of lettuce (the spring-summer season)

Combination	N	P	K	Ca	Mg	Na	Fe	Mn	Zn	Cu
	[% in d.w.]						[mg · kg^{-1} d.w.]			
Control	2.18 ab	0.51 ab	4.10 a	1.85 a	0.31 ab	0.49 b	99.2 a	214.6 c	49.9 a	6.40 b
EM-A[1]	2.13 a	0.54 bcd	4.80 c	2.00 c	0.33 b	0.36 a	176.3 d	180.8 ab	81.0 cd	6.00 a
EM-A[2]	2.13 a	0.49 a	4.54 b	1.87 ab	0.32 ab	0.54 bc	150.3 c	232.7 d	76.7 bc	5.95 a
EM-5[1]	2.39 d	0.52 abc	4. 95 d	1.94 b	0.33 b	0.57 c	153.5 c	181.3 ab	83.7 d	6.10 a
EM-5[2]	2.31 c	0.55 cd	5.09 e	2.12 d	0.32 ab	0.60 c	179.6 d	175.3 a	74.7 b	5.80 a
EM-A[3]	2.23 b	0.57 d	5.06 e	1.89 ab	0.28 a	0.60 c	133.6 b	183.2 b	85.6 d	5.90 a

Explanation: EM application method: [1] irrigation, [2] spraying, [3] seed inoculation.

Macroelements. In both cultivation cycles after the application of EM the content of iron in lettuce leaves tended to increase, but there were significant differences between the application methods. There were multidirectional changes in the content of manganese – the tendencies were divergent in the research cycles. Like with iron, the content of zinc increased significantly after the application of EM. The tendency was observed in both research cycles. Simultaneously, the content of copper tended to decrease in the spring-summer season. There were multidirectional changes in the autumn cycle.

Table 2

The influence of EM on the chemical composition of lettuce (the autumn season)

Combination	N	P	K	Ca	Mg	Na	Fe	Mn	Zn	Cu
	[% in d.w.]						[mg · kg^{-1} d.w.]			
Control	2.10 a	0.47 a	4.15 a	1.92 a	0.27 a	0.57 c	101.7 a	240.9 c	54.4 a	5.6 a
EM-A[1]	2.17 a	0.56 b	4.95 bc	1.95 a	0.32 b	0.42 a	194.1 d	155.9 a	93.9 d	6.3 b
EM-A[2]	2.12 a	0.51 a	4.45 ab	1.87 a	0.28 a	0.51 b	156.2 c	235.4 c	91.3 d	5.8 a
EM-5[1]	2.43 b	0.49 a	4.87 bc	1.89 a	0.34 b	0.49 b	147.3 c	187.6 b	78.9 b	5.7 a
EM-5[2]	2.28 ab	0.53 b	5.02 c	2.03 a	0.29 ab	0.59 c	193.8 d	179.1 b	71.5 b	6.1 b
EM-A[3]	2.21 a	0.56 b	5.07 c	1.99 a	0.27 a	0.56 c	124.7 b	173.4 b	82.6 c	6.2 b

Explanation: EM application method: [1] irrigation, [2] spraying, [3] seed inoculation.

The preparations containing Effective Microorganisms (EM) are mixtures of active microorganisms of biological origin. EM is composed of lactic acid bacteria (*Lactobacillus casei*, *Lactobacillus plantarum*, *Streptococcus lactis*), photosynthetic bacteria (*Rhodopseudomonas palustris*, *Rhodobacter sphaeroides*, *Rhodobacter spae*), yeasts (*Saccharomyces albus*, *Candida utilis*), actinobacteria (*Streptomyces albus*, *S. griseus*) and moulds (*Aspergillus oryzae*, *Mucor hiemalis*) [3, 7]. The application of EM may influence the chemical composition of soil or the substrate in which plants grow. In consequence, plants' nutrition may be affected. According to Mayer et al [25], nitrifying bacteria increase the content of nitrogen, whereas actinobacteria affect the content of phosphorus. This thesis was generally confirmed in the study conducted by Gorski and Kleiber [13], but in many cases the changes observed by the authors were multi-directional.

The research proved the significant influence of Effective Microorganisms on the chemical composition of the aerial parts of lettuce. The research findings positively correspond to earlier data reported by Fraszczak et al [26], who investigated the possibility to apply EM to basil (*Ocimum basilicum* L.) grown in a peat substrate. Sahain *et al* [20] reported that apple-tree leaves collected from the plants treated with EM contained more N, P, K, Mn, Fe and Zn. The yield of plants also improved. Changes in the chemical composition of crops treated with EM may be caused by changes in the chemical composition of the substrate [13] Simultaneously, Gorski and Kleiber [13] applied EM to ornamental plants (roses and gerberas) and observed that their yield improved significantly. The highest yield of flowers was noted when EM was applied to the roots. Simultaneously, the diameter of rose flowers and the number of gerbera leaves increased. The positive effect of EM on the yield of horse-shoe pelargoniums was also proved [27]. The plants treated with EM had more buds and flowers and they bloomed earlier. Studies conducted by other authors [12, 28] also confirmed the positive effect of EM on the yield of other plans species, *ie* saffron and strawberry. Javaid [17] reported that EM applied to peas significantly affected the formation of root nodules. Available sources [29] also point to the stimulating effect of preparations containing EM on the utility parameters (vigour, germination capacity) of beetroot, carrot, tomato and cucumber seeds.

EM may have positive effect on plants' health. Boliglowa and Glen [30] claim that when winter wheat was sprayed with an EM solution, the plants were effectively protected from glume blotch (*Septoria nodorum*) and tan spot (*Drechslera tritici-repentis*). Stepien and Adamiak [31] reported that the EM-1 preparation applied to spring and winter wheat significantly inhibited the development of septoria leaf blotch (*Mycospharella tritici*), glume blotch (*Septoria nodorum*), wheat leaf rust (*Puccinia recondita*), barley powdery mildew (*Blumeria graminis*) and Fusarium ear blight (*Fusarium* spp.). Okorski and Majchrzak [32] proved that EM applied to peas significantly limited the occurrence of *Fusarium* fungi in seeds.

The stimulating effect of microorganisms on the growth of plants may be caused by their secretion of secondary metabolites, growth hormones, phytochelatins, organic acids and B vitamins [19]. Daly and Stewart [3] reported that microorganisms might stimulate some physiological processes in plants. This thesis was confirmed by Xu

Hui-lian et al [15], who proved that EM stimulated photosynthesis and influenced the content of vitamin C and sugars in tomato fruits. Vitamin C plays a key role in controlling the redox potential in plants and it acts directly as an antioxidant capturing reactive oxygen species and as a co-factor for many enzymes [33]. The study by Sahain et al [20] proved that the plants treated with EM had higher content of chlorophyll in leaves and better plant growth parameters (the emergence of new roots, the root length and diameter and the leaf area).

Conclusions

The research proved the influence of EM on the chemical composition of aerial parts of lettuce.

As far as macroelements are concerned, there was higher content of phosphorus after seed inoculation with EM-A and spraying with EM-5 in the spring-summer season. The tendencies were confirmed in the autumn cycle (there was significantly higher content after the irrigation of plants with EM-A).

There was significantly higher content of potassium in lettuce leaves (as compared with the control combination) and there was a simultaneous general increasing tendency in the content of calcium.

The highest content of magnesium was noted when the plants were irrigated with EM. The inoculation of seeds resulted in the lowest content of this element. There were similar tendencies at both terms.

As far as microelements are concerned, the content of iron (significant differences between the methods of application) and zinc tended to increase. Apart from that, there was significant diversification in the content of sodium in lettuce leaves. The smallest content was observed when the plants were irrigated with EM-A. The content was significantly higher in the other combinations. Changes in the content of nitrogen, manganese and copper were multidirectional.

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WPŁYW ZASTOSOWANIA EFEKTYWNYCH MIKROORGANIZMÓW NA SKŁAD CHEMICZNY SAŁATY UPRAWIANEJ POD OSŁONAMI

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Abstrakt: Celem przeprowadzonych badań była ocena wpływu zastosowania Efektywnych Mikroorganizmów (EM) na zawartość składników pokarmowych w liściach sałaty (*Lactuca sativa* L. 'Sunny') uprawianej pod osłonami, w okresie wiosenno-letnim i jesiennym. Określono wpływ następujących form aplikowania EM: dokorzeniową, dolistną oraz poprzez zaprawianie nasion. Przy stosowaniu EM dokorzeniowo, rośliny podlewano w zależności od kombinacji 1% roztworem preparatu EM-A lub EM- 5 (250 ml cieczy na 1 roślinę). Do opryskiwania dolistnego wykorzystano wyżej wymienione środki, w stężeniu 1%. Zaprawianie nasion przeprowadzano bezpośrednio przed wysiewem (moczenie przez 30 minut w 10% roztworze preparatu EM-A). W okresie wegetacji przeprowadzono 4-krotnie zabiegi opryskiwania lub podlewania roślin, w odstępach 3 dniowych. W kombinacji kontrolnej nie stosowano Efektywnych Mikroorganizmów. W przeprowadzonych badaniach wykazano wpływ zastosowania EM na zawartość składników pokarmowych w liściach sałaty. Stwierdzono poprawę odżywienia roślin azotem po stosowaniu preparatu EM-5 poprzez podlewanie i opryskiwanie roślin. Jednocześnie wykazano istotną poprawę odżywienia roślin fosforem przy zaprawianiu

nasion preparatem EM-A oraz opryskiwaniu roślin środkiem EM-5, w obu terminach uprawy i dodatkowo przy podlewaniu roślin (EM-A) w cyklu jesiennym. Zastosowanie preparatów EM wpływało istotnie na zwiększenie zawartości potasu w liściach sałaty (w relacji do kontroli), przy równoczesnej generalnej tendencji wzrostowej zawartości wapnia (istotnej dla podlewania obydwoma preparatami oraz opryskiwania środkiem EM-5 w terminie wiosenno-letnim). Największą zawartość magnezu oznaczono w przypadku podlewania roślin EM, a najmniejszą dla zaprawiania nasion (tendencje w obydwóch terminach uprawy były zbliżone). W przypadku mikroskładników w obu cyklach uprawowych po zastosowaniu EM zaobserwowano istotną tendencję wzrostową zawartości żelaza oraz cynku w liściach sałaty, a poziom wzrostu był zróżnicowany w zależności od sposobu aplikowania preparatów.

Słowa kluczowe: Efektywne Mikroorganizmy (EM), sałata, składniki pokarmowe, makroskładniki, mikroskładniki

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THE SYNTHESIS OF COMPOUNDS RICH IN -SH GROUPS IN PLANTS OF SELECTED *Silene vulgaris* ECOTYPES DEPENDING ON NICKEL DOSE

SYNTEZA ZWIĄZKÓW BOGATYCH W GRUPY -SH W ROŚLINACH WYBRANYCH EKOTYPÓW *Silene vulgaris* W ZALEŻNOŚCI OD DAWKI NIKLU

Abstract: The main goal of the research was to determine the influence of increasing nickel doses (0, 30, 60, 90 mg · kg[1]) on the content of -SH groups in plants of selected *Silene vulgaris* ecotypes originating from other habitats.

In the experiment we used *Silene vulgaris* seeds from calamine regions of Upper Silesia (an area next to the *Szopienice* foundry in Katowice), a location connected with serpentinite deposits exploitation (Wiry landmass) and natural ecotype seeds from an area uncontaminated by heavy metals (Gajkow near Wrocław). The analyzed plant material had -SH groups but there were clearly more in the above-ground parts of the selected *S. vulgaris* ecotypes. Only in the case of Gajkow ecotype *S. vulgaris*, from a location without nickel, the number of thiol groups was clearly higher in roots. Chemical analyses of plant material showed that along with the increase of nickel dose, the –SH group concentration also increased in the shoots of *Silene vulgaris* of all ecotypes. However, the concentration was the highest with the dose of 60 and 90 μM Ni for Gajkow ecotype plants from an area with a naturally low content of heavy metals. On the other hand, the smallest number of thiol groups deposited in shoots was found in Wiry ecotype plants from a habitat rich in nickel (serpentinite spoil tip).

Keywords: *Silene vulgaris*, ecotype, nickel, -SH groups, phytochelatins

Introduction

Nickel belongs to a group of heavy metals forming Earth's crust. Its occurrence is strictly connected with alkaline igneous rocks and sedimentary clay rocks [1]. Nickel content in Earth's soils varies strongly between 3 and 1000 mg · kg^{-1} [1]. The mean content of this element, calculated for Polish soils, is 9 mg · kg^{-1} [1], but serpentinite soils (naturally rich in nickel compounds) in Lower Silesia visibly surpass this value.

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Studies conducted by Zolnierz [2] in the selected serpentinite massifs have shown concentrations exceeding 3000 mg · $kg^{-1.}$.

Nickel is a necessary nutrient for plants. However, the demand for this element is small and is only 0.1–5 mg [1, 3–5]. Nickel is an important micro-element ensuring proper growth and development of plants by activating the enzymes of numerous metabolic processes [3–5]. Nickel is a part of the active site of urease, an enzyme hydrolyzing urea, and thus plays a significant role in providing urea for plants and takes part in the metabolism of urea derivatives and in binding atmospheric nitrogen by soil bacteria. In plants nickel is also a part of hydrogenases and nickel deficiencies lead to leaf tip necrosis and urea accumulation in cells [3–5].

Nickel belongs to transition elements and its bioavailability for plants, particularly on contaminated soils, is big and increases along with its increased concentrations in the environment [3–5]. Nickel absorbed by a plant moves from roots to above-ground parts. Nickel ions are very rarely transported in a plant in a free form. After entering the symplast they are almost instantaneously complexed by low molecular ligands (chelatine ligands) [3–5]. Among the essential nickel ion chelates there are organic acids (citric acid, malic acid, malonic acid, oxalic acid), amino acids (*eg* histidine, which forms coordination complexes with Ni ions), metallothioneins, low molecular mass proteins rich in cysteine and phytochelatins (metallothiol, low molecular poly-peptides) [3–5]. The above-mentioned compounds enable easy transport of nickel in the plant and decrease its toxicity, which is important when the intake of this metal is too big [3–5]. The mechanism of nickel's toxic influence on plants has not been fully explained yet.

The toxic influence of nickel is related, for instance, to the occurrence of chlorosis connected with excluding iron from physiological functions. The excess of nickel also stops the functioning of enzymes containing iron, *eg* catalase and peroxidase and, after excessing critical concentration, disrupts photosynthesis [3–5] due to the influence on the transport of electrons and the decrease in chlorophyll.

Researchers are now interested in plants which adapted to life in highly contaminated areas or areas naturally rich in heavy metals, *eg* post-industrial areas, post-mining areas or metal-rich soils [6–10]. In Poland areas where surface soils are naturally rich in nickel compounds are limited to serpentinite soils particular for Lower Silesia and formed of serpentinite rocks [2]. Serpentinite rock habitats are characterized by many unfavorable properties (high and potentially toxic concentrations of nickel, chromium and magnesium; low content of phosphorus, potassium and nitrogen; low humidity; highly alkaline pH) and, thus, have unique vegetation [2].

Post-mining and post-industrial serpentinite locations (spoil tips, quarries) of Lower Silesia are characterized by low biodiversity and dispersion and *Silene vulgaris* is one of the few taxa on the floristic content list [6–8].

The species is a good indicator of heavy metal contamination in soils and its presence was determined both on areas naturally rich in heavy metals and on locations where human influence caused the heavy metals contamination [8–12].

In literature one may find descriptions of this species' unique adaptation capabilities leading to the emergence of separate ecotypes adapted to extremely unfavorable habitat

conditions. Apart from *Silene vulgaris* ecotypes resistant to lead and zinc, there are also ones tolerating the excess of cadmium and copper [8–12].

Comparative studies conducted by Koszelnik-Leszek and Bielecki [13] have shown that *Silene vulgaris* ecotypes originating from different habitats (with high and naturally low heavy metal contents in soil) differed from one another in morphological features – plant height, leaf lobe width – and a nickel experiment has shown different reactions of chosen ecotypes to the metal. Serpentinite ecotype plants, as compared to other ecotypes, accumulated more nickel.

One of the most important parts of plant's defense against heavy metal poisoning is the synthesis of phytochelatins, as it is believed that the synthesis of these compounds is one of the key detoxification mechanisms [3–5, 13–20]. Phytochelatins, which are structurally derivative of glutathione, are formed on the basis of a particular dipeptide – Glu-Cys (2–11 times repetition) and their synthesis occurs enzymatically and is activated by metal ions, among others Cd^{+2}, Pb^{+2}, Cu^{+2}. Due to numerous thiol groups (-SH) of cysteine residue they are capable of successfully bond and deactivate ions of many heavy metals [13–20].

That is why the aim of this paper is to determine the level of glutathione and phytochelatins through counting thiol groups in the selected ecotypes of *Silene vulgaris* growing in the conditions of raised soil nickel levels.

The conducted studies will allow us to determine if the selected *Silene vulgaris* ecotypes have a clear increase in synthesized phytochelatins and glutathione along with the increased levels of soil nickel and which of the selected ecotypes have a higher or smaller predilection for these compounds.

Materials and methods

The plants of three *Silene vulgaris* ecotypes were the study material. The *Gajkow* ecotype comes from a habitat with naturally low nickel contents near Gajkow village located to the south-east of Wroclaw [13]. The *Szopienice* ecotype grows in an area located 250 m from pollution emitter, a foundry in Katowice (Huta Metali Niezelaznych *"Szopienice"*) in Upper Silesia [18]. The *Wiry* ecotype grows on a small spoil tip connected with serpentinite rock exploitation in Lower Silesia, near Wiry village located at the western base of Sleza Mountain [13].

Pot experiment

The seeds of three *Silene vulgaris* were planted in pots filled with autoclaved, moist garden soil. After two weeks the plants of each ecotype were to separate pots. The plants were grown in glasshouse conditions with sunlight exposure. After 8–9 weeks a part of the plants of each ecotype were studied biometrically and the other part had their roots cleaned thoroughly and planted in pots filled with Hoagland and Arnon nutrient solution [21] (0.5 dm^3). After the plants acclimatized themselves, nickel sulfate was added to the nutrient solution so that the concentration of nickel reached 0, 30, 60,

and 90 μM (each dose was applied in 4 repetitions). The experiment lasted two weeks. In that time, the nutrient solution was regularly aerated. After seven days the nutrient solution was exchanged for a new one and nickel sulfate was again added in the same doses. After two weeks the experiment was finished, the plants gathered and preserved for further chemical analyses. The compounds rich in -SH groups were marked in the sample materials using Wojcik and Tukiendorf method [16] and the technique of High-performance liquid chromatography (HPLC). The number of -SH groups was measured from standard curve for glutathione.

Results and discussion

Phytochelatins are of particular interest in research into plant tolerance levels. It is believed that the synthesis of these compounds is one of the essential heavy metals detoxification mechanisms in plants [13–20].

The structure of phytochelatins is formed by numerous thiol groups (-SH) bonding heavy metals and thus limiting their negative impact on the plant [13–20].

The essence and definition of plant tolerance to heavy metals is the ability to sustain heavy metal ion homeostasis on cellular and tissue level [20]. Currently it is believed that sustaining heavy metal ion homeostasis in plants is connected with complexing leaf and root cells in cytosol. In case of the phytochelatin complex (PCS) – metal is transported to the vacuole, where it is separated from other cellular organelles [13–20].

In the analyzed plant material (under- and above-ground parts of selected *S. vulgaris* ecotypes – Fig. 1) the study revealed the presence of -SH groups but they were clearly more numerous in the above-ground parts (Fig. 1). Only in the case of the *Gajkow* ecotype from a nickel free location (control) the number of thiol groups was clearly higher than in the roots (Fig. 1).

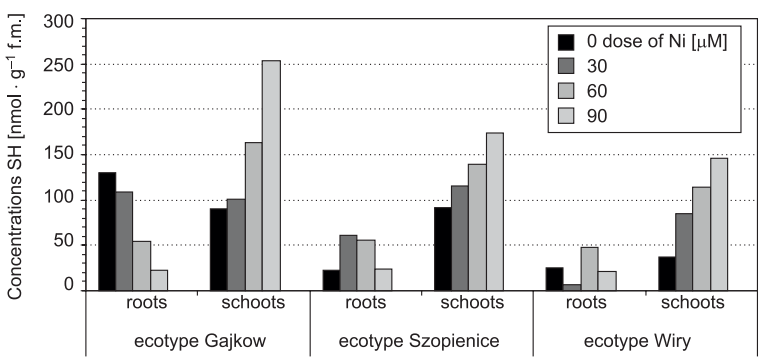

Fig. 1. The concentration of -SH groups in roots and shoots in *Silene vulgaris* ecotypes (e.)

Chemical analyses of plant material has shown that along with the increase of nickel dose the concentration of -SH groups in the shoots of *Silene vulgaris* also increased in all ecotypes. However, the most groups were detected (mainly in the dose of 60 and 90 μM Ni) in the *Gajkow* ecotype coming from a location with naturally low heavy metal

content. What is more, the smallest amount of thiol groups was deposited in the shoots of *Wiry* ecotype originating from a habitat rich in nickel (a serpentinite spoil tip).

Earlier studies by the author [13] conducted on the same ecotypes and in the same experiment conditions with increasing nickel doses have shown that the *Wiry* ecotype accumulated more nickel in the above-ground parts than the *Gajkow* ecotype, which, in the same experiment conditions, accumulated the least of it.

The previous [13] and current results obtained by the author may suggest that, as it is implied by Seth et al [19], in stress conditions caused by hydroponic cultivation with the addition of nickel, phytochelatins take part in metal detoxification in plants with low tolerance to metals (*Gajkow* ecotype). On the other hand, in plants with higher tolerance to metals (*Wiry* ecotype), the role of phytochelatins in detoxification in high-stress conditions seems to have a smaller impact on their tolerance despite the induction of phytochelatins synthesis [12]. According to De Knecht et al [12], though, the amount of phytochelatins does not always indicate the tolerance to metals. Analyses of selected ecotypes' roots (Fig. 1) have shown that only in the case of the *Gajkow* ecotype the number of thiol groups regularly decreased along with nickel dose. In the cases of other ecotypes there was no clear dependence.

A clear increase in the number of thiol groups in the shoots of experimental plants as compared to the roots was determined by Wojcik and Tukiendorf [16] because after 14 days of hydroponic cultivation of *Arabidopsis* with cadmium dose they observed a clear increase in phytochelatins in above-ground parts in comparison to the roots (particularly with higher doses).

Summing up the thiol group number in roots and shoots (Fig. 2a–d) it has been determined that, despite the nickel dose, the natural *Gajkow* ecotype deposited the most of them and the *Wiry* ecotype from the serpentinite spoil tip – the least.

However, the natural ecotype plants grown in control conditions had the number of thiol groups comparable to that of plants from locations with 30 and 60 μM nickel doses (Fig. 2a–c). It is important to remember that the nutrient solution itself (control location) is a source of easily available metal forms. With the highest dose – 90 μM Ni – the analyzed parts of the natural ecotype of *Silene vulgaris* have shown a visible increase in -SH groups.

In the cases of other ecotypes from locations with higher metal concentrations (Szopienice and Wiry) it was determined that the phytochelatins content in plants from control locations was lower in comparison to their concentrations in plants growing in raised nickel conditions (Fig. 2a–d). In these ecotypes it was also observed that with lower nickel doses – 30 and 60 μM (Fig. 2b, 2c) – the content of thiol groups was balanced (within the ecotype) but with a higher dose – 90 μM (Fig. 2d) – it was clearly higher than in the other nickel combinations. The increasing number of phytochelatins (usually) increasing along with the nickel dose confirm the research by Gawel et al [17] where the authors note that phytochelatins concentration reflects the current level of heavy metal availability in the environment.

The recorded lower content of thiol groups (phytochelatins and glutathione) in *Silene vulgaris* of the *Wiry* and *Szopienice* ecotypes as compared to the *Gajkow* ecotype (Fig. 2a–b) may be connected with their habitats of origin, respectively one rich and one

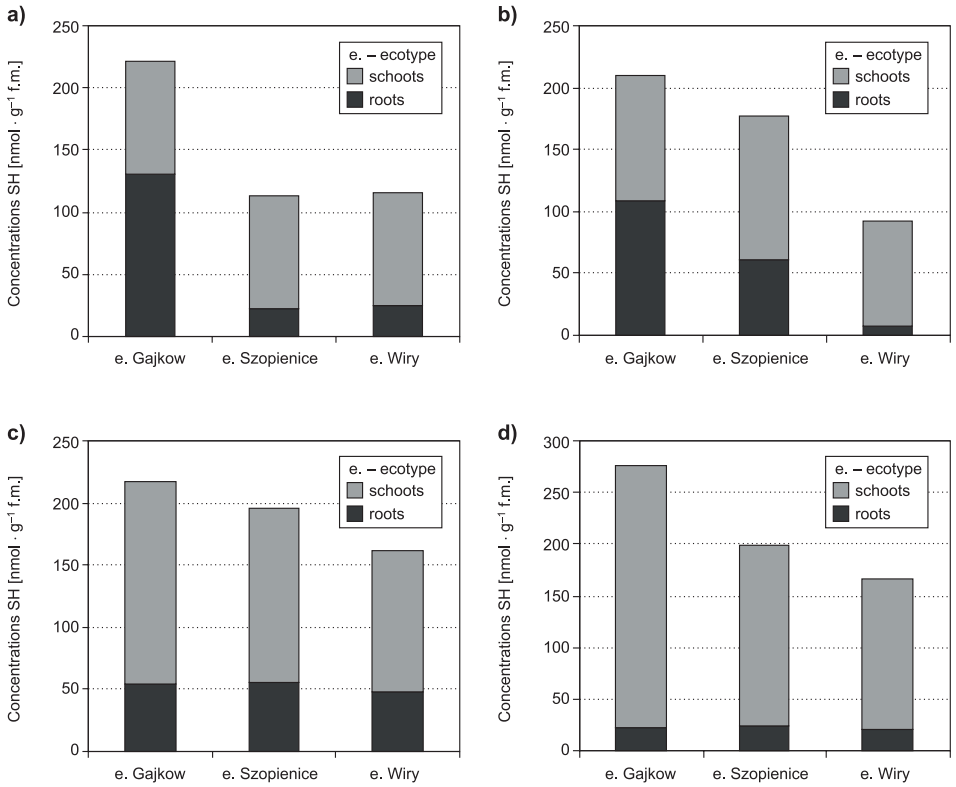

Fig. 2. The concentration of -SH groups in selected *Silene vulgaris* ecotypes depending on nickel dose: a) control, b) 30 μM Ni, c) 60 μM Ni, d) 90 μM Ni

contaminated with heavy metals. And so, in both cases, the results may reflect the adaptation to growth in conditions with higher metal contents and, consequently, weaker reaction to nickel and other metals in the nutrient solution manifesting in lower levels of synthesized phytochelatins and glutathione.

Conclusions

One of the most important elements of response to stress caused by heavy metals is the synthesis of phytochelatins and glutathione resulting in higher concentrations of thiol groups in plant material. The concentration of phytochelatins reflects the current level of heavy metal availability in the surrounding environment and determines the physiological stress level in plants. Therefore, the obtained results are a contribution to further research into these compounds which may be used as, for instance, bio--indicators of heavy metal contamination in plants.

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SYNTEZA ZWIĄZKÓW BOGATYCH W GRUPY -SH W ROŚLINACH WYBRANYCH EKOTYPÓW *Silene vulgaris* W ZALEŻNOŚCI OD DAWKI NIKLU

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Abstrakt: Głównym celem badań było określenie wpływu wzrastających dawek niklu (0, 30, 60, 90 mg · kg^{-1}) na zawartość grup -SH w roślinach wybranych ekotypów *Silene vulgaris* pochodzących z odmiennych siedlisk.

W eksperymencie wykorzystano nasiona *Silene vulgaris* pochodzące z obszarów galmanowych Górnego Śląska (obszar przyległy do huty „Szopienice" w Katowicach), związanych z eksploatacją złóż serpentynitowych (zwałowisko w Wirach) oraz nasiona ekotypu naturalnego, z terenu nie zanieczyszczonego metalami ciężkimi (Gajków koło Wrocławia).

W analizowanym materiale roślinnym, stwierdzono obecność grup -SH z tym jednak, że wyraźnie więcej było ich w częściach nadziemnych wybranych ekotypów *S. vulgaris.* Jedynie w przypadku roślin *S. vulgaris* ekotypu Gajków pochodzącego z obiektu bez niklu, liczba grup tiolowych była wyraźnie wyższa w korzeniach.

Analizy chemiczne materiału roślinnego wykazały również, że wraz ze wzrostem dawki niklu wzrastała koncentracja grup -SH w łodygach *Silene vulgaris* wszystkich ekotypów z tym że najwięcej ich zliczono przy dawce 60 i 90 mg Ni, dla roślin ekotypu Gajków pochodzącego z obszaru o naturalnie niskiej zawartości metali ciężkich. Natomiast wyraźnie najmniej grup tiolowych zliczono w częściach nadziemnych *S. vulgaris* ekotypu Wiry pochodzącego z siedliska zasobnego w nikiel (hałda serpentynitowa).

Słowa kluczowe: *Silene vulgaris*, ekotyp, nikiel, grupy -SH, fitochelatyny

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ANTLER MALFORMATIONS OF CERVIDAE SPECIES IN OPOLE VOIVODESHIP

DEFORMACJE POROŻA U JELENIOWATYCH W WOJEWÓDZTWIE OPOLSKIM

Abstract: Hunting Law regulations strictly determines which males of quarry species may be harvested during the season. The age and the antlers of the individual play here an important role. The exceptions are the individuals with malformed and long spiked antlers, that is in a form significantly different from the desirable forms described in guidelines by the Chief Hunting Council. Anomalies in shape, structure and size of antlers are obligatory condition for harvesting the individual. It is generally accepted that such individuals are weaker, less valuable, have defective genes, are sick or injured, and are dangerous for conspecific during the rut. The scientific explanations for the development of an antler abnormalities point out many different factors, including the environmental ones. For many years antlers are used to determine the environmental pollution by heavy metals accumulated in it's bone tissue what gives precise annul data. The aim of this work was to check whether the frequency of antlers deformation in cervidae species present in the Opole Voivodeship correlate in any way with ontogenetic features (age and body weight), population features (density and size of population) and environmental factors (woodiness, competition). Results could set new directions in researches for causes of antler malformations in cervidae family.

Keywords: antler malformations, cervidae

Introduction

Antlers developed by the cervidae family spieces are unique bone structures in animal world. They are the fastest growing bones known to science. Also they are shed annually, and than regrown [1]. They play different roles: as a weapon – to compete other males during rut or to defense from predators, as a tool – to dig in snow for food, and reproductive – to attract females [2]. Their shape and structure are consistent amongst cervidae family making it easy to recognize a species by the antler itself. Some slight differences might occur at the level of population and individuals (different shape and angle of beams, the number of tines), yet both beams are usually symmetric and

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absolutely consistent to a species. From hunting point of view, the bigger and heavier the antlers are – the more valuable the trophy is. Hunting low regulations in Poland strictly describe which individuals might be harvested according to their age and form of their antlers. There are only two exceptions to that regulations [3], usually given together: the so called malformed antler and long spiked ("myłkus" and "szydlarz" in Polish) [4].

Although much is known about the molecular mechanisms involved in regrowing the antler [5–6] the reasons why malformations occur are still unclear and varied. Most explanations are focused on endocrine disruptions [7–11] or point out injuries to skull or legs [8, 12–15], but there are other possible causes like diet [16, 17], lack of trace elements [18–21], heritability [22, 23] or even stress factors like fear [24]. We can suspect that at the end most of these factors can lead to endocrine disruptions. Surprisingly there are no direct links in the literature between environment pollution and malformations of the antler, although some knowledge [25] emerges from studying the chemical content of the shed antlers which are used in environmental pollution monitoring giving precise data from fallowing years [26–28].

The purpose of this study was to analyze frequency of antler malformations amongst cervidae in Opole voivodeship for any correlations with interpopulation or environmental factors and choice of most suitable species for further studies.

Materials and methods

Species and samples

Four species of cervidae family are present in Opole voivodeship, the Red deer (*Cervus elaphus*), Fallow deer (*Dama dama*), Roe deer (*Capreolus capreolus*) and Moose (*Alces alces*). Except for the Moose all these species are harvested by local Hunting Association. Among them the most common are the Roe deer and rarest is the Fallow deer. Data achieved from Opole Hunting Association describes species, date of harvesting, hunting area, body weight, antlers weight, antlers type, number of tines and age of the individual. In total: 3363 for Roe deer, 953 for Red deer and 133 for Fallow deer specimens were analyzed.

Hunting grounds and season

Opole voivodeship lies in southern-western Poland and share border with Czech Republic. Main geographical barriers are the A1 highway crossing the region (with very narrow, improperly designed animal transitions) and Odra river. Much of the wildlife management in Opole voivodeship is made by local Hunting Association on 144 out of 156 hunting grounds (it approximately covers 92% of Opole voivodeship) and these were taken into account. Hunting grounds were different in many aspects: the woodiness, area size, human density etc. All specimens were harvested in 2012/2013 hunting season. In some hunting grounds all species were present, in some (open fields) only one, mostly the Roe deer.

Statistical methods

Correlations between frequencies of malformations in hunting grounds and inter-population or environmental factors were checked using Pearson correlation coefficient (r) or Spearman Rho correlation coefficient in case of lack of normal distribution of data. Statistical significances of differences between values of studied data were checked using t-Student test. The null hypothesis was always that there are no differences between compared groups of specimens in particular feature.

Results

Frequency of antler malformations in different species

Red deer. 953 specimens were harvested in 2012/2013 hunting season of which 74 had malformed or spiked antlers (7.66%). Frequencies of antler malformations in different hunting grounds were in a range of 0.0 up to 0.5 with average value of 0.07.

Fallow deer. 133 specimens were harvested in 2012/2013 hunting season of which 11 had malformed or spiked antlers (8.27%). Frequencies of antler malformations in different hunting grounds were in a range of 0.0 up to 0.4 with average value of 0.10.

Roe deer. 3363 specimens were harvested in 2012/2013 hunting season of which 390 had malformed (without spiked ones) antlers (11.6%). Frequencies of antler malformations in different hunting grounds were in a range of 0.0 up to 1.0 with average value of 0.13.

Antler malformations according to body weight and age

Red deer. The average body weight of harvested stags with properly formed antlers was 111 ± 25 kg and 104 ± 24kg for ones with antler malformations, while average age was 5.4 ± 2.5 years and 5.32 ± 2.3 years respectively. Correlation between body weight and age in whole population is only positively moderate with $r = 0.52$. Differences between body mass in stags with proper and malformed antlers, despite their age and time of harvesting, were significant, and weight of stags with proper antlers was bigger (d (difference of mean) = 6.40, SD (standard deviation) = 25, p (probability value) = 0.035). Although number of harvested stags with malformed antlers decline along with their age, the percentage of them in whole harvested population in particular age changes, reaching its maximum in the age of 10 years (Fig. 1).

Fallow deer. The average body weight of harvested bucks with properly formed antlers was 50 ± 10kg and 55 ± 16kg for ones with antler malformations, while average age was 4.5 ± 1.7 years and 4.5 ± 2.1 years respectively. Differences between body mass in bucks with proper and malformed antlers, despite their age and time of harvesting, were not significant ($d = –4.98$, SD = 10, $p = 0.33$). There is also no differences in age in both groups at significance level of $p = 0.01$. The number of harvested stags with malformed antlers as well as percentage of them among all harvested bucks in particular age changes, reaching its maximum in age of 8 years (Fig. 2).

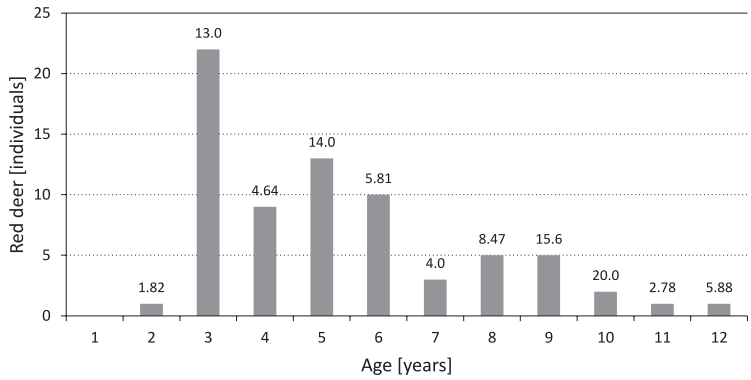

Fig. 1. Stags with malformed antlers harvested in 2012/2013 hunting season with their percentage share among all harvested stags (values given above columns)

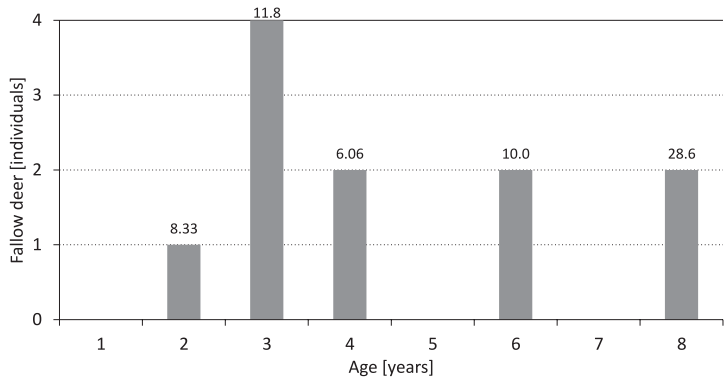

Fig. 2. Bucks of Fallow deer with malformed antlers harvested in 2012/2013 hunting season with their percentage share among all harvested bucks (values given above columns)

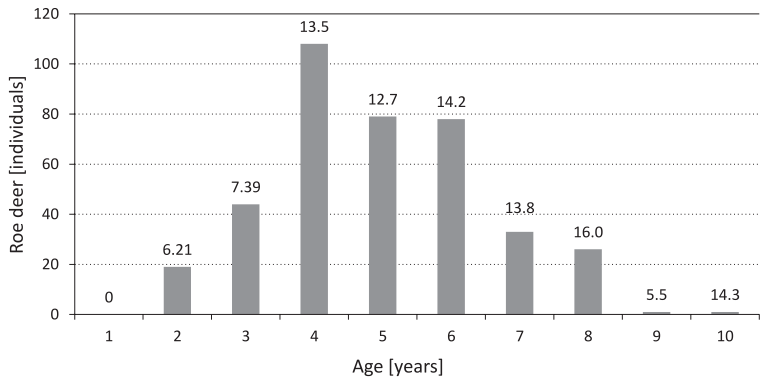

Fig. 3. Bucks of Roe deer with malformed antlers harvested in 2012/2013 hunting season with their percentage share among all bucks (values given above columns)

Roe deer. The average body weight of harvested bucks with properly formed antlers was 16.1 ± 2.1 kg and 16.4 ± 1.9 kg for ones with antler malformations, while average age was 4.9 ± 1.5 years and 4.6 ± 1.5 years respectively. Differences between body weight in bucks with proper and malformed antlers, despite their age and time of harvesting, were significant (t – Student test, $p < 0.01$). The number of harvested stags with malformed antlers as well as percentage of them among all bucks in particular age changes reaching its maximum in age of 10 years (Fig. 3).

Density of population and frequency of antler malformations

The Roe deer were harvested on all hunting grounds managed by Opole Hunting Association, the Red deer were harvested on 101 hunting grounds and Fallow deer on 20. The annual hunting management plans are based on the size of population of a particular species, therefore we can assume that the number of harvested specimens reflects directly the size of local populations. Knowing the exact size of hunting grounds [29] in Opole voivodeship ranging from 3196 ha to 12273 ha (average 5628.3, median 5311.5) and the fact that Roe deer males are faithful to their summer grounds [30] we can calculate a value reflecting density of it's local populations. In case of a Red deer we can only assume that migration among males is low (except during the rut) due to flat surface of Opole voivodeship, abundance of food, isolation of Niemodlinskie Forest and none/very low predation risk [31, 32]. Literature about migrations of Fallow deer in Poland is limited, yet, especially in Opole voivodeship where this species have the oldest populations established in hunting grounds managed by National Forestry [33], we can be sure of slow migration based on population density from more to less populated hunting grounds. Considering that low migration does not significantly effect the condition of local populations of studied species we can seek for correlation between value reflecting it's densities and frequency of antler malformations. Results of such calculations showed that in 2012/2013 hunting season there were no correlations between density of the Roe deer and frequency of antler malformation ($r = –0.005$, $n = 131$), neither for a Red deer ($r = 0.027$, $n = 99$) and Fallow deer ($r = –0.037$, $n = 20$). Also size of local populations of all three species did not correlated with antler malformation frequency among Roe, Red and Fallow deer ($r = –0.047$, $r = –0.054$ and $r = 0.164$, respectively).

Woodiness of hunting grounds and antler malformations

Average woodiness for Opole voivodeship is 29,9% and woodiness of hunting grounds of Opole Hunting Association varies in a range from 0% up to 84% [34, 35]. There are two main forest complexes: Niemodlin Forest to the south from Odra river and Stobrawsko-Turawskie Forest to the north. To check the correlation between woodiness and antler malformation I used a Spearman Rho correlation coefficient due to lack of normal distribution of both parameters. For Roe deer, which inhabits hunting grounds with forest cover from 0% to 84% (average 24,9%), antler malformations were not significantly associated with woodiness ($r = 0.009$). The Fallow deer was harvested

on hunting grounds with woodiness from 6% to 84% (average 43,6%), but in this species studied feature was only weakly, negatively associated with woodiness (r = –0.151). The Red deer was harvested on hunting grounds with woodiness from 1% to 84% (average 30.0%) and it was the only species in which antler malformations are significantly, but moderately, associated with the woodiness of hunting grounds (r = 0.34).

Mutual occurrence of antler malformations among studied species

All three cervidae species coexist in almost all hunting grounds across Opole voivodeship, but except for Roe deer, not everywhere they are harvested. The mutual occurrence of antler malformations in particular hunting grounds average value for specific species are shown below (Table 1).

Table 1

Mutual occurrence of malformations in studied species on particular hunting grounds with frequencies higher than average value for specific species

Game species	Frequencies of antler malformations					
	Min. value	Max. value	Average value	Median value	No. of hunting grounds	Mutual occurrence
Roe deer	0.0	0.37	0.13	0.12	73	13
Fallow deer	0.0	1.0	0.10	0.0	4	2
Red deer	0.0	0.50	0.07	0.0	31	13

Discussion

Antler malformations occur in all harvested cervidae species present in Opole voivodeship. The Roe deer has the lowest value of maximal frequency of antler malformation in particular hunting ground, yet it has the highest percentage share of all specimens with abnormalities in it's whole population. Moreover it is present in all hunting grounds no matter the forest cover and is the most numerous, thus it is the most suitable species for further studies on antler malformations.

If occurrence of antler malformation would be genetically conditioned and would manifest year after year since the first grown antler one could expect that highest share of specimens with antler malformations should be in first years of their life. Later, their share should decline due to higher chance for hunters to harvest such specimens until their share in whole population would drop significantly. But is seems it does not work that way. The percentage of harvested bucks and stags with malformed antlers in particular age did not decline as they got older. This might be explained by three possibilities: 1) genetics condition the occurrence of malformations but additional trigger is needed/malformation would not necessarily manifest since youth, 2) the chances for harvesting specimens with antler malformations are not associated with

their share in whole population, 3) occurrence of malformations is conditioned by environmental or population factors. As heritability of antlers shape and size in cervidae species has not been proven to be very high [22, 23, 36] and been rather correlated with age [37] first explanation, based on genetic conditioning, is rather insufficient (moreover hunters and shed antler collectors can easily recognize the specimen year after year by shape of its antlers, so the new antlers are rather similar to previous ones). The chance for harvesting the specimens with antler malformations according to their share in whole population should rather be considered as high. Hunters have plenty of time to track down such specimens (Roe deer before the rut, Red and Fallow Deer during rut), especially in field-type hunting grounds. Although total number of harvested specimens with visible antler malformations was highest in age of 3–4 for all studied species, that not happened with their share in population across different age. In case of all three studied species the highest percentage share of specimens with antler malformation in population was at age of 10, 8 and 8 for Red, Fallow and Roe deer respectively. It rather seems that environmental or population factors play the key role in occurrence of abnormalities in antlers while stags and bucks are getting older.

Stags with proper antlers harvested in 2012/2013 hunting season were significantly heavier than ones with malformed antler in the same age. This may support statement that specimens with antler malformation are of poorer condition yet contrary results in case of Roe deer and no significant differences in Fallow deer make it rather doubtful or these association vary in different species or across years. Differences between species might depend on different biology, behavior and type of preferred habitat. In most suitable species for further studies on that phenomena, the Roe deer, it seems that bucks with antler malformations are heavier and one can suspect, that in better condition, what need further investigation.

Antlers are secondary sex characteristics and are used to fight with other conspecific during the rut. This may lead to many wounds on skull. In fact, such injuries often lead to antler malformations [2, 12–15], especially to accessory antlers [9]. As males compete for females and territories one can suspect, that the higher density of local population of a deer species, the higher the chance for confrontation during rutting time. Therefore the chance for injuries across the so called “antlerogenic territory” leading to occurrence of accessory antler should be also greater. This may explain the growing share of specimens with antler malformations in Red and Fallow deer since gaining maturity. But neither size or density of local populations did not correlated with antler frequencies in all studied species. Thus, the factor which is responsible for antler malformations in older age of studied species is rather environmental than based on these two, important population characteristics.

Forest cover plays important roles for deer species providing food, shelter, peace etc. Only the Roe deer is adopted to live all year long on open fields, the two other studied species need forests to thrive. The weak, negative correlation between antler malformations and woodiness in case of Fallow deer might occur due to small sample. The moderate, positive in Red deer is surprising. Perhaps it is somehow associated with diet or injuries to growing and soft tissue of antler from branches, fences, and dense shrub?

In case of Roe deer woodiness has nothing to antler malformations what makes this species even more suitable for further studies.

Reasons for antler malformations to occur need investigations from longer periods. If lack of correlation between interpopulation factors and antler malformations would be proven across the years in particular population, than environmental (anthropogenic?) factors might play an important role in this phenomena.

Conclusions

The most suitable species for further studies on antler malformation is a Roe deer. The occurrence of antler malformations does not decline along with age in all studied species and it seems that environmental or inter-population factors determine occurrence of abnormalities in antlers, rather than heritability. Moreover two important population factors: density and it's size does not correlate with frequency of antler malformations. The woodiness of hunting grounds, in case of a Roe deer and Fallow deer, also does not correlate with studied feature. Only in Roe deer, the specimens with antler malformations were significantly heavier than does with proper antlers. Frequency of antler malformations need further investigation from across the several years and involving different factors which may induce its occurrence.

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DEFORMACJE POROŻA U JELENIOWATYCH W WOJEWÓDZTWIE OPOLSKIM

Samodzielna Katedra Biotechnologii i Biologii Molekularnej, Wydział Przyrodniczo-Techniczny
Uniwersytet Opolski, Opole

Abstrakt: Regulacje Prawa Łowieckiego ściśle określają, które samce zwierzyny płowej mogą zostać pozyskane w danym sezonie. Kluczową rolę odgrywają tu wiek oraz forma poroża danego osobnika. Wyjątek stanowią tzw. „myłkusy" oraz „szydlarze", czyli osobniki mające poroże w formie istotnie odbiegającej od wytycznych określanych przez Naczelną Radę Łowiecką. Anomalie w kształcie, budowie i rozmiarach poroża stanowią obligatoryjny warunek do pozyskania mającego je osobnika, którego uważa się za niepożądanego w łowisku. Powszechnie uznaje się takie osobniki za słabsze, mniej wartościowe, mające wadliwe geny, chore lub zranione, a także niebezpieczne dla innych w okresie rui. Naukowe uzasadnienia powstawania anomalii w porożu jeleniowatych wskazują na wiele różnych czynników, w tym środowiskowych. W ostatnich latach podjęto również prace nad określaniem skażenia środowiska bytowania jeleni metalami ciężkim w oparciu o oznaczanie tych pierwiastków w rogowej tkance poroża, które w cyklu rocznym jest nakładane i następnie zrzucane. Celem tej pracy było sprawdzenie, czy częstość występowania deformacji w porożu u jeleniowatych na terenie województwa opolskiego w jakikolwiek sposób koreluje z cechami osobniczymi (wiek oraz waga tuszy), wewnątrzpopulacyjnymi (zagęszczenie i wielkość populacji) oraz środowiskowymi (lesistość, konkurencja). Wyniki mogą wyznaczyć nowe kierunki w badaniach nad przyczynami powstawania deformacji w porożu jeleniowatych.

Słowa kluczowe: myłkus, jeleniowate, poroże

Varia

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