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Elwira TOMCZAK[1*] and Anna DOMINIAK[2]

A BRIEF HISTORY OF THE WATER SUPPLY SYSTEM AND WATER QUALITY IN THE CITY OF LODZ

HISTORYCZNE ZMIANY STRUKTURY SIECI WODOCIĄGOWEJ NA TLE UTRZYMANIA STANDARDÓW WODY PITNEJ DLA MIASTA ŁODZI

Abstract: Poland's third largest city, Lodz, underwent rapid industrial and demographic growth in the 19th and 20th centuries, followed by a steep decline over the last three decades. This paper describes how the water supply system has been adapted over the last century to meet these challenges, and in particular how the source of water (surface or underground) and structure of the supply system has been adapted to maintain drinking water quality. The Lodz water supply has been managed since 1925 by the firm Zaklad Wodociagow i Kanalizacji Sp. z o.o. The water supply system was designed by the Englishman William H. Lindley (in 1909), but because of World War I and the global depression that followed work began only in 1934. After World War II further deep wells were constructed, followed by a pipeline network and treatment plant. A 50-kilometre pipeline bringing surface water from the Pilica River was completed in 1955, followed by the Sulejowski Reservoir on the same river (1968–1973). Algal blooms on the reservoir presented a major challenge, and deep wells were turned to as a solution. By 2010 Lodz had 58 deep well intakes, so that in 2013 it was no longer necessary to take taking surface water from the Sulejowski Reservoir.

Keywords: Lodz water supply system, exploitation of water, drinking water quality

Introduction

Poland's third largest city, Lodz (2011 population 728,892; metropolitan population 1,428,600), is located in the drainage basin of the Vistula and Oder (Odra) rivers, in the catchment area of two substantial watercourses: the Bzura, a tributary of the Vistula, and the Ner, a tributary of the Oder. This richly watered area was favourable to settlement and the emergence of the first textile manufactories. The rapid development of Lodz as a textile centre in the nineteenth and early twentieth centuries resulted in the intensive exploitation of the region's natural water resources and a drastic decline in the

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quality of groundwater. The industrialisation of the city, river regulation works, and the changing course of the rivers together with the drainage of wetlands led to major changes in the hydrographical map of the region.

The creation of an urban water supply system satisfied the basic needs of residents and industry, but the continued growth of the city necessitated a search for ample and reliable (albeit distant) sources of drinking water and the construction of an infrastructure of wells, water treatment plants and a network of distribution pipelines. New technologies were constantly developed to ensure the inhabitants were supplied with the appropriate amount of water of the highest possible quality.

In 1909 the Lodz city authorities commissioned the renowned English civil engineer Sir William Heerlein Lindley (1853–1917) to design water and sewerage systems for the city. He pointed out the following potential sources of water:

1. Water-bearing chalk layers of the Upper Jurassic in the area north of Tomaszow Mazowiecki – Sulejow, and subterranean water in the vicinity of Lodz.
2. Water-bearing layers of the Quaternary period to the northwest of the Pilica River and the south and southwest of Lodz.
3. Surface water from the Pilica River.

Besides the needs of industry, which had its own water intakes, Lindley estimated the city’s future daily water requirements at 154,000 cubic metres, assuming a million inhabitants each consuming 130–200 litres per day.

Lindley’s design was ready by 30 October 1909, and in November plans at a scale of 1:10,000 of water mains and sewers were completed using the then novel technique of heliography.

In 1901, Lodz had a population of 310,000, but in 1908 the Russian authorities incorporated several villages and suburbs within the city boundaries, so that by 1911 the population exceeded 450,000. During the First World War the German occupying authorities conducted another large incorporation of lands within the city limits in 1915. Lodz was then the most densely populated city in Poland, with 10,439 inhabitants per square kilometre. A large number of these people were reliant solely on water from individual shallow wells, which were often contaminated. The sub-surface aquifer supplying these wells was slowly running dry as a result of widespread demand and ever increasing consumption from numerous textile factories.

Development of the Lodz water supply network

In 1925 the operation, treatment and distribution of the Lodz water supply was entrusted to the Municipal Water and Wastewater Company (ZWiK). However, as a result of World War I and the global economic crisis, work on the Lodz water supply system began only in 1934, under the supervision of the engineer Stefan Skrzywan, and the cheapest possible version – based on deep wells – was chosen.

The initial phase required the drilling of five wells and construction of a 100-km network of pipes. A pumping station and iron removal facility was to be built at Dabrowa connected by pipelines to wells and a drinking-water reservoir at Stoki, from which, via three water mains and a network of distribution pipes, water would be fed by gravity to the city.

A capital intensive part of the project was the underground reservoir at Stoki, built between 1935 and 1937 (which continues to serve the city to this day). It consists of huge twin tanks, each square in plan with sides of 60 metres, and 7 metres in height, with a water level of up to 5 metres, giving a capacity of 15,000 cubic metres per tank. The structure is an architectural marvel, with the vaulting of each tank consisting of 100 brick domes supported on 81 columns. Each dome is a brick structure with a square base of 5.5 metres along the edge.

At the outbreak of the Second World War in 1939 work had progressed as follows: only three wells had been drilled, work on a filtration and pumping station had commenced, 9.4 km of mains pipeline had been built, along with an equalizing tank at Stoki with a capacity of 30,000 cubic metres and about 62 km of distribution pipes. However, the municipal water system had not yet undergone its first trials.

It was only after the war, towards the end of 1945, that 204 properties (lived in by almost 20,000 people) were connected to the municipal water system. By the end of 1949, 21.6 km of municipal pipelines had been built, along with connections to individual buildings. At the same time a further three wells reaching down to the Upper Cretaceous aquifer were put into operation.

The increasing number of domestic connections was, however, fast creating a water shortage. A temporary solution was to build street hydrants and bring water into the city in tanker trucks. Even so, water rationing had to be introduced in 1950: Lodz was the only city in Poland to have daily quotas for private customers – initially 80 litres, later 100 litres per person.

In 1951 the government took the decision (long awaited by the city authorities) to commence work on a pipeline linking Lodz to an intake on the Pilica River at Tomaszow Mazowiecki. Construction of the first leg of the pipeline took three years. At this time a stretch of 2 km of the banks of the Pilica river were channelled and a weir was built to regulate flow. A pumping station was built to bring the water to a treatment plant about 1.5 km away. Here the river water was treated, and when crystal clear flowed through a special pipeline, halfway to Lodz, to a pumping station at Rokiciny, and then on to the reservoir at Stoki. In this way the water supply was increased to 92,000 cubic metres per day.

The next stage was the creation of a reservoir at Smardzowice, created by building a large dam on the Pilica River to produce a 17 km-long artificial lake, with a capacity of 75 million cubic metres and an area of 23 km^2. The lake was filled with water in May 1973, and a pumping station was built nearby in the village of Bronislawow. Six months later, more than 132,000 cubic metres of water were being drawn every day from the reservoir (in 1977, daily abstraction reached nearly 258,000 cubic metres, the highest from a single source during the entire history of the Lodz water supply system).

In the late 1990s the idea emerged of gradually replacing surface water with underground water from wells drilled in the vicinity of the lake. Seven wells were drilled in Bronislawow drawing water from the Upper Cretaceous aquifer. These have a capacity of more than 18 million cubic metres per year (50,000 cubic metres daily).

In 2000 the Lodz water system was modernized to streamline operations. In view of the topography of the area in which the city lies, the system was divided into two pressure zones. The northern part is gravity fed with water from the reservoir at Stoki. Here the water is a mainly sourced from deep wells together with a small amount of Pilica River water from the intake at Tomaszow Mazowiecki. The southern part of the city, which is smaller both in terms of area and population, is supplied entirely from deep wells in Bronislawow.

In all there are 43 wells within the city or on its outskirts; in 22 of these wells the water is so good that it requires no treatment. Lodz also makes use of eight wells in Rokiciny, seven in the vicinity of the Sulejowski Reservoir, and the intake on the Pilica River at Tomaszów Mazowiecki, though by 2010 the total contribution of the latter to the Lodz water supply amounted to only about 10 % [1].

Sulejowski Reservoir

Over the years the intensive development of industry in Lodz and overuse of the deep wells led to a fall in the groundwater level by as much as 100 metres. A “dried out” cone of depression was gradually forming beneath the city draining moisture from as far as 20 km away. To allow the water table to replenish itself the decision was taken to build a massive reservoir, over 40 km away, on the Pilica River.

The original concept was to bring the water to Lodz in a 42-km open canal. But this idea was quickly abandoned. Instead, work began on the construction of a pipeline using seamless, large diameter (1.6 m and 2.2 m) steel pipes. The contract could not be fully meet by Polish steel mills, so sections of the pipe were imported from Germany. At the same time the reservoir was built. It was a huge project that involved the relocation of 70 farms, the felling of 1600 hectares of forest, and the transfer of 1.5 million cubic metres of soil. The city waited impatiently for its new source of water. In the 1970s demand for water was increasing by 10,000–20,000 m^3 annually. Again, rationing was introduced, this time on industry.

After the reservoir was put into use it was not long before a number of complications arose and the water quickly became polluted. The original designs had called for a whole network of sewage treatment plants and a safe buffer zone to be put into operation around the reservoir. Unfortunately, funds ran out for the improvement of local sewerage facilities. Although a protection zone was established both directly and indirectly around the water intake, the planned sewage collectors were never built. Additionally, no attempts were made to prevent the unrestricted influx of thousands of holidaymakers treating the drinking-water reservoir as a place for swimming and sailing.

The Suleowski Reservoir covers a huge area but is very shallow – averaging just 3.5 metres – and it did not cope well with the rapid proliferation of algae during sunny weather. From the beginning it has been inadequately protected from the eutrophication process “fed” by nitrates and phosphates draining into it from the local area. Special varieties of herbivorous fish were introduced into the lake but these did not help. The first bloom of cyanobacteria was observed in 1975, a year after the reservoir was filled. Further blooms followed in successive years. Before the late 1980s this was not recognised as a danger to human health. It was only in the 1990s that the serious health risk created by these blooms was identified. Quickly, the decision was taken to close bathing areas during algal blooms.

Research showed that cyanobacterial toxins in the water could be effectively removed during the purification process. Maximum effort was made in bringing water drawn from the reservoir up to legal standards. A treatment plant (at Kalinko) was daily consuming dozens of tons of chemicals, ranging from chlorine, aluminium sulphate and activated silica to lime and activated carbon. It quickly became clear that, in its existing form, the reservoir would never be a source of good clean water.

In the search for an alternative source of drinking water for Lodz it was decided to build deep wells near the Sulejowski Reservoir, at Bronislawow. In all seven wells were successively drilled down to the Upper Cretaceous aquifer, providing a total daily capacity of 50,000 m^3.

Changes in the quality of Lodz drinking water, 1945–2013

To reflect the influence that the source of water has on the quality of the tap water delivered to customers over this period, five indicators of water quality are taken into account in this paper: colour, turbidity, dissolved oxygen, and the content of iron and manganese [1–5]. These are typical of the water quality parameters inspected by the ZWiK laboratory.

Colour and turbidity

The parameters most visible to the consumer are colour and turbidity. Considerable changes have been observed over the years, depending on the original source of the water. Between 1945 and 1960 there were no national regulations providing standards for these parameters, and so no data is available for this early period. When in 1965 the Minister of Health made it obligatory to analyse drinking water for colour and turbidity, it emerged that Lodz water obtained from the Pilica River had parameters close the

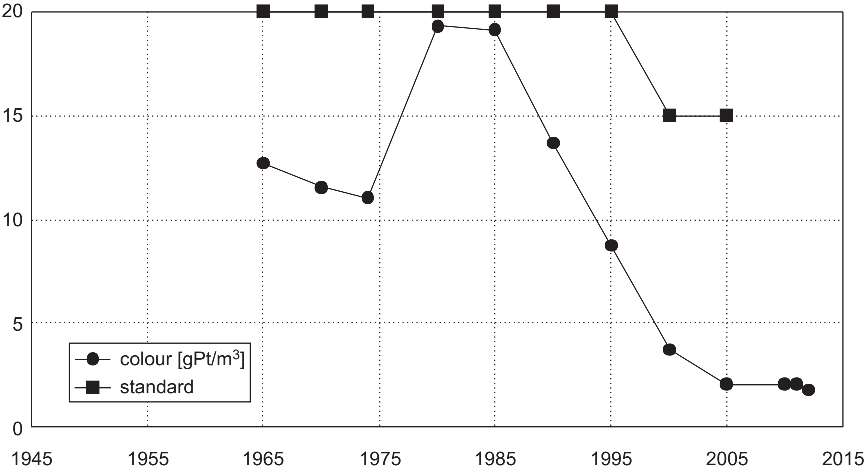

Fig. 1. Colour of Lodz drinking water since 1965

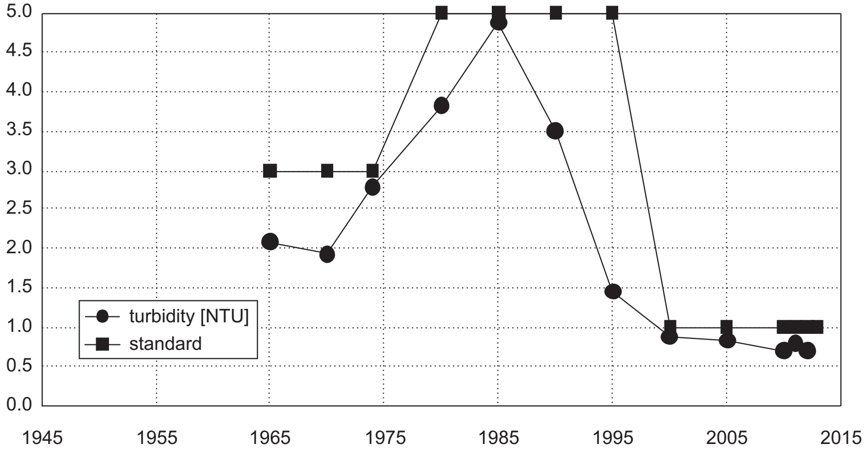

Fig. 2. Turbidity of Lodz drinking water since 1965

maximum legally permitted limits. After the intake on the Sulejowski Reservoir was brought into use the parameters remained at a high level. It was only in 2000, when the majority use of surface water was replaced in favour of underground water the colour and turbidity of Lodz drinking water improved, as is illustrated in Figs. 1 and 2.

Dissolved Oxygen (DO)

The amount of oxygen dissolved in the drinking water is an indicator of the quantity of organic and certain inorganic compounds in the water. For a long time there was no binding standard, and it was only in 2000 that the health minister made it compulsory to record this parameter. Since 1945 dissolved oxygen in the Lodz water system has been

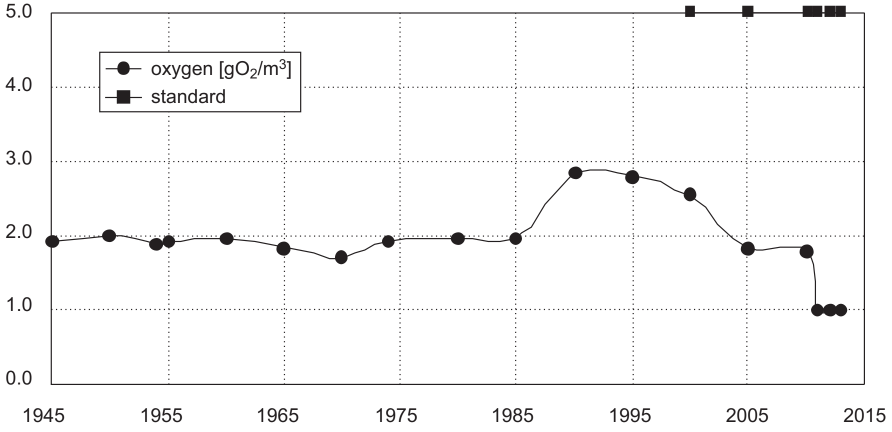

Fig. 3. Concentration of dissolved oxygen in Lodz drinking water since 1945

measured with $KMnO_4$, but only for internal technological analysis when assessing the dose of chlorine required for disinfection. The highest values of DO were recorded in the 1985–2000 period, that is when surface water was being sourced from the Sulejowski Reservoir, which was closely associated with blooms of *cyanobacteria* [6] (Fig. 3).

Iron and manganese

The presence of iron and manganese in drinking water is characteristic of water sourced from underground: surface waters generally do not contain these elements except in very small quantities. Figures 4 and 5 illustrate how the concentration of iron and manganese in drinking water is dependent on the source of the raw water.

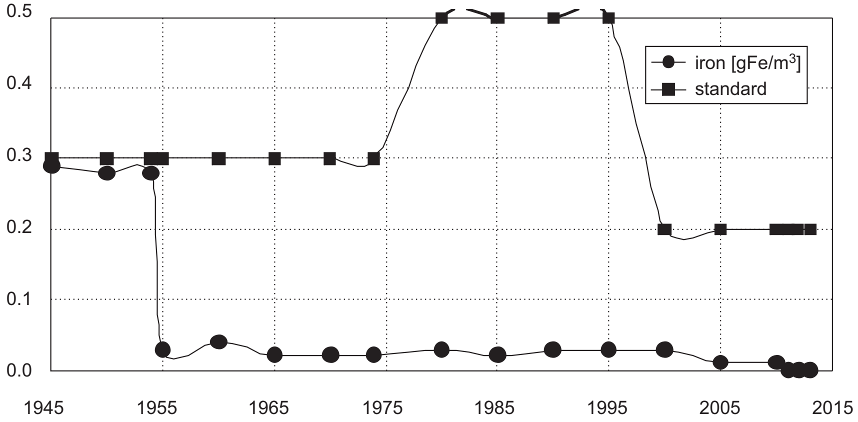

Fig. 4. Iron content of Lodz drinking water since 1945

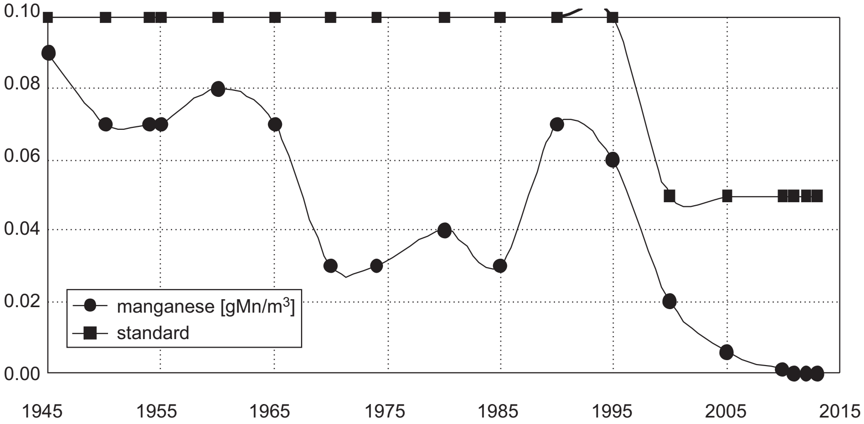

Fig. 5. Manganese content of Lodz drinking water since 1945

Very high concentrations were recorded between 1945 and 1954, when relatively shallow wells were in use.

Over the 1945–2000 period, *ie* when surface water was being used, the problem of high levels of iron and manganese was gradually eliminated. Now, thanks to the abstraction of water from greater depths and the use of new treatment technologies, the concentration of these elements is below the detection limits of current testing techniques.

The prospects for Lodz water production and distribution

The current economic and commercial situation of Lodz is having a significant affect on the economics of operating the municipal water supply. Due to the lowering of demand since 1989 there has been a steady decline in the amount of water supplied to the network – from 350,000 cubic metres per day in 1989 to about 90,000 in 2013. In the meantime, the size of the network has increased by about 260 km. Thus, while the capacity of the network has grown, the amount of water actually flowing in the network has fallen significantly [7, 8]. As a result, any change in the direction of water flow in the pipeline caused by emergencies or necessary adjustments to the operation of the network may result in deterioration of the quality of water supplied to the public [9]. The priority now is to maintain the system in a good state of repair, and to counteract the phenomenon of secondary pollution of water in the network.

Work is now in progress on pilot studies to examine microbial contamination in water networks using a luminescence method [10], based on the detection of ATP (*adenosine triphosphate*) present in all living cells. This will give immediate results for bacteriological tests (instead of the minimum 24-hour delay by traditional methods) and allow an immediate response in the event of biological contamination of Lodz drinking water [11].

Another plan is to improve the monitoring of the water supply system to obtain real-time data on the operation of the municipal network, specifically flow rate, flow direction, pressure and turbidity. This will allow a quick response to operational faults and should eliminate or reduce the effects of adverse incidents. Data from the new monitoring system will be used to build a mathematical model of the hydraulics of the pipe network, which will allow pipes of appropriate diameters to be chosen to adjust the water flow to current and future needs.

Summary

Since it was created in the Lodz water commercial system it has continuously evolved to meet the city's changing needs. The quality of Lodz drinking water has varied over the years depending on the type of water used – surface, underground or mixed. This was especially true between 1945 and 2000 when the priority for the Lodz waterworks was to satisfy the needs of a growing town in terms of quantity of water supplied. This translated into a reduction of quality – in particular, high levels of dissolved oxygen and turbidity. The colour of water at the tap was a common cause of customer complaints, especially while water was being drawn from the Sulejowski Reservoir.

The quality of Lodz tap water continues to be inspected regularly. Water is sampled at treatment stations and when drawn into the water system, and also directly from pipelines at nearly a hundred locations throughout the city. Dozens of parameters are tested at the company's laboratories.

A further safeguard is provided by so called bio-monitors – fish (perch) and mussels that live in aquariums at eleven different facilities belonging to the firm. Water intended for Lodz's households flows continuously through the aquariums, and perch and mussels are extremely sensitive to changes in water quality and to pollutants that might pose a danger to human health. Since 2009 the mussels have been monitored by special equipment that provides constant information on their wellbeing.

Since 2000, that is since the closure of the largest water-consuming industrial customers, the problem has mainly been one of the excess of water in the system. Besides the ageing infrastructure at intake points and treatment plants, dealing with the oversize pipelines and stagnant water in the network has been a challenge. These problems have largely been overcome so that today the water drawn from deep wells is some of the best drinking water supplied to residents anywhere in Poland.

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HISTORYCZNE ZMIANY STRUKTURY SIECI WODOCIĄGOWEJ NA TLE UTRZYMANIA STANDARDÓW WODY PITNEJ DLA MIASTA ŁODZI

Wydział Inżynierii Procesowej i Ochrony Środowiska
Politechnika Łódzka

Abstrakt: Projekt łódzkiej sieci wodociągowej, wykonany przez najlepszego europejskiego fachowca W. Lindleya, powstał już w 1909 r. Realizację rozpoczęto w 1934 r., przy współudziale polskiego inżyniera S. Skrzywana. Po II wojnie światowej dokonano wiercenia dalszych studni głębinowych i zbudowano system wodociągowy oraz stację uzdatniania wody. Zbudowano 50 km rurociągu Tomaszów–Łódź (1955 r.), zbiornik retencyjny na Pilicy (1968–1973) i kolejne studnie głębinowe. W 2010 r. istniało już 58 ujęć wód podziemnych dlatego też w 2013 r. zapadła decyzja o rezygnacji z ujmowania wody powierzchniowej z Zalewu Sulejowskiego. Celem pracy było przedstawienie miejsc pobierania wody i struktury sieci wodociągowej, której budowa ulegała zmianom w zależności od potrzeb i rozwoju dużego miasta, w powiązaniu z uzyskiwaniem wody pitnej najwyższej jakości. Piecze nad eksploatacją i dystrybucją nieprzerwanie od 1925 r. sprawuje Zakład Wodociągów i Kanalizacji Sp. z o.o. w Łodzi.

Słowa kluczowe: wodociąg łódzki, eksploatacja wody, jakość wody pitnej

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Małgorzata RAFAŁOWSKA[1*] and Katarzyna SOBCZYŃSKA-WÓJCIK[1]

ANALYSIS OF TEMPERATURE CONDITIONS AND DISSOLVED OXYGEN CONCENTRATIONS IN THE PILWA BAY (LAKE DOBSKIE)

ANALIZA WARUNKÓW TERMICZNO-TLENOWYCH WÓD W ZATOCE PILWA (JEZIORO DOBSKIE)

Abstract: This study was carried out in the Pilwa Bay of Lake Dobskie located in the mesoregion known as the Land of Great Masurian Lakes, Gizycko district. Temperature and oxygen conditions in the western, central and eastern (connected to Lake Dobskie) parts of the Pilwa Bay were studied by analyzing the vertical distribution of temperature and dissolved oxygen concentrations in the winter and summer seasons of three consecutive years (2005–2007). Measurements were performed using the WTW OxiTop OC 100 system with automatic temperature compensation.

During winter stagnation, the highest dissolved oxygen content was noted in the top water layer under ice cover, and oxygen concentrations varied widely between years. An analysis of temperature and oxygen profiles revealed an insignificant temperature difference of approximately 1–2 ^{o}C between the surface and bottom layers of water, which indicates that the studied bay was not characterized by a summer stratification pattern typical of deep water bodies.

Keywords: temperature and oxygen profiles, thermal stratification, bay

Introduction

Water heats and cools slowly, and it exhibits smaller changes in temperature than air. The above implies that lake ecosystems provide a more supportive environment for the growth of aquatic organisms than land habitats.

The temperature of surface (standing) waters is determined by the depth of the water body, the movement and mixing of waters. Temperature is a key factor conditioning the metabolic activity of aquatic organisms. It affects the solubility of chemical compounds in water, and it supports thermal stratification. The accumulation of thermal energy in

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lakes is determined by various processes, mostly direct absorption of solar radiation, transfer of energy from the sediment layer, transfer of energy from the surrounding land and the metabolic activity of organisms.

During summer stagnation, surface waters in the epilimnion zone are mixed by the wind, and they are characterized by relatively uniform temperature and oxygen concentrations. The thickness of the epilimnion layer is determined mostly by weather conditions in a given year, the size of the water body and its location relative to wind direction. At a certain depth of the metalimnion (transition zone), temperature and oxygen concentrations decrease rapidly to form meta- and oxycline zones. Temperature and oxygen levels decrease fairly uniformly with an increase in depth. The highest water density is noted at 4 ^{o}C, but such temperatures are observed only in deep lakes. In the benthic zone, oxygen concentrations approximate zero. In shallow and highly eutrophic water bodies, an absence of oxygen may be observed already at smaller depths. A reverse temperature gradient is noted in the winter. Water is cooler in the surface layer, its temperature increases with depth, along with a simultaneous drop in oxygen concentrations. In transitional periods between direct stratification and inverse stratification in the winter, homothermia, the vertical mixing of the water column takes place in the spring and fall [1].

The aim of this study was to determine the effect of winter and summer seasons on selected physicochemical properties of water in the Pilwa Bay.

Materials and methods

This study was carried out in the Pilwa Bay of Lake Dobskie located in the mesoregion known as the Land of Great Masurian Lakes, Gizycko district. Lake Dobskie constitutes the western part of the Mamry Lake complex, and it is a typical ground moraine formation. The lake has an area of more than 1776 ha, and the bay occupies 52.98 ha with an average depth of 1.36 m and a well-developed shoreline (K = 1.88). The shoreline development index (K) is the quotient of shoreline length (l) and the circumference of a circle with an area equal to the lake's area (A_0):

$$K = \frac{l}{2\sqrt{\pi A_0}}$$

The index is a denominate number equal to or higher than 1 [2]. In its present shape, the bay is a only a remnant of the former section of Lake Dobskie that spanned an area of more than 100 ha. The western part of the Pilwa Bay is supplied by watercourses draining catchment areas which are semi-intensively farmed and intensively fertilized. Sections of Lake Dobskie's catchments are exposed to nitrogen runoffs from farmland.

The Pilwa Bay was selected for the study because it receives outflow water from agricultural catchments and functions as an ecotone by preventing the penetration of undesirable contaminants into the main basin of Lake Dobskie. However, long-term human pressure has led to intense eutrophication in the bay.

Vertical distributions of temperature and dissolved oxygen levels were measured in the Pilwa Bay in the winter and summer seasons of the three-year experiment (2005–2007). Measurements were performed using the WTW OXI Top OC 100 oxygen sensor with automatic temperature compensation. In the summer, the Secchi disc method was used to monitor water transparency. Additional measurements were performed to determine electrolytic conductivity, oxygen saturation and pH of water. To account for Pilwa Bay's bathymetric features, shape and varied character, the analyzed water body was divided into three sections based on the direction of water flow: western (554), central (554A) and eastern part which is connected to the main basin of Lake Dobskie (553) (Fig. 1).

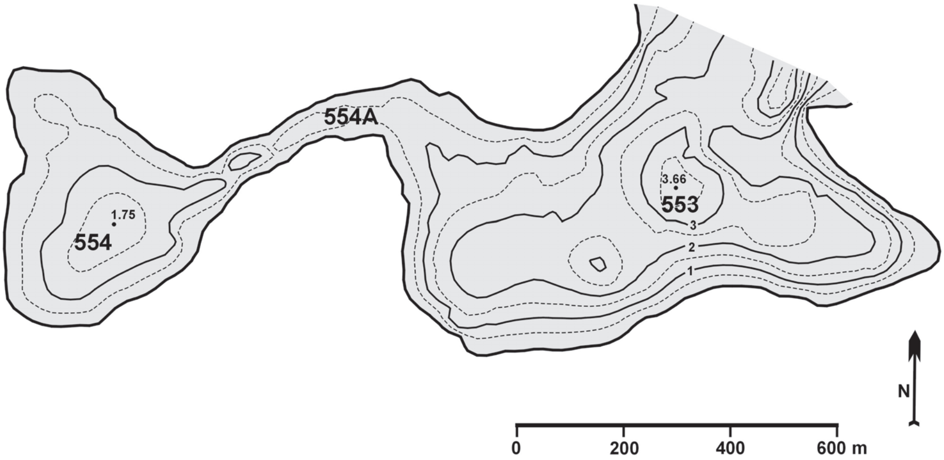

Fig. 1. Sampling sites

Results and discussion

Dissolved oxygen concentrations varied widely due to changes in weather conditions, including temperature of ambient air and water. Inverse stratification was observed in the winter when the temperature of surface water approximated 0 °C, and it increased gradually below the depth of 0.5 m to reach around 2 °C at the bottom (Fig. 2–4). Since water circulation is the main source of oxygen supply in lakes, dissolved oxygen concentrations were generally consistent with water mixing dynamics [3]. During winter stagnation, the highest dissolved oxygen levels were noted in the upper water layer under ice cover, and oxygen concentrations varied extensively between years. In the milder winters of 2005 of 2007 (average January temperatures of 0.6 and 2.6 °C, respectively), oxygen concentrations in the surface layer fluctuated between 3.68 and 13.21 $\text{mgO}_2 \cdot \text{dm}^{-3}$. In the winter of 2006 when average January temperature reached –4.3 °C, oxygen concentrations in the western and central parts of the bay were determined in the range of 0.27 to 0.32 $\text{mgO}_2 \cdot \text{dm}^{-3}$, *ie* below the minimum temperatures for fish survival. The critical concentrations of dissolved oxygen

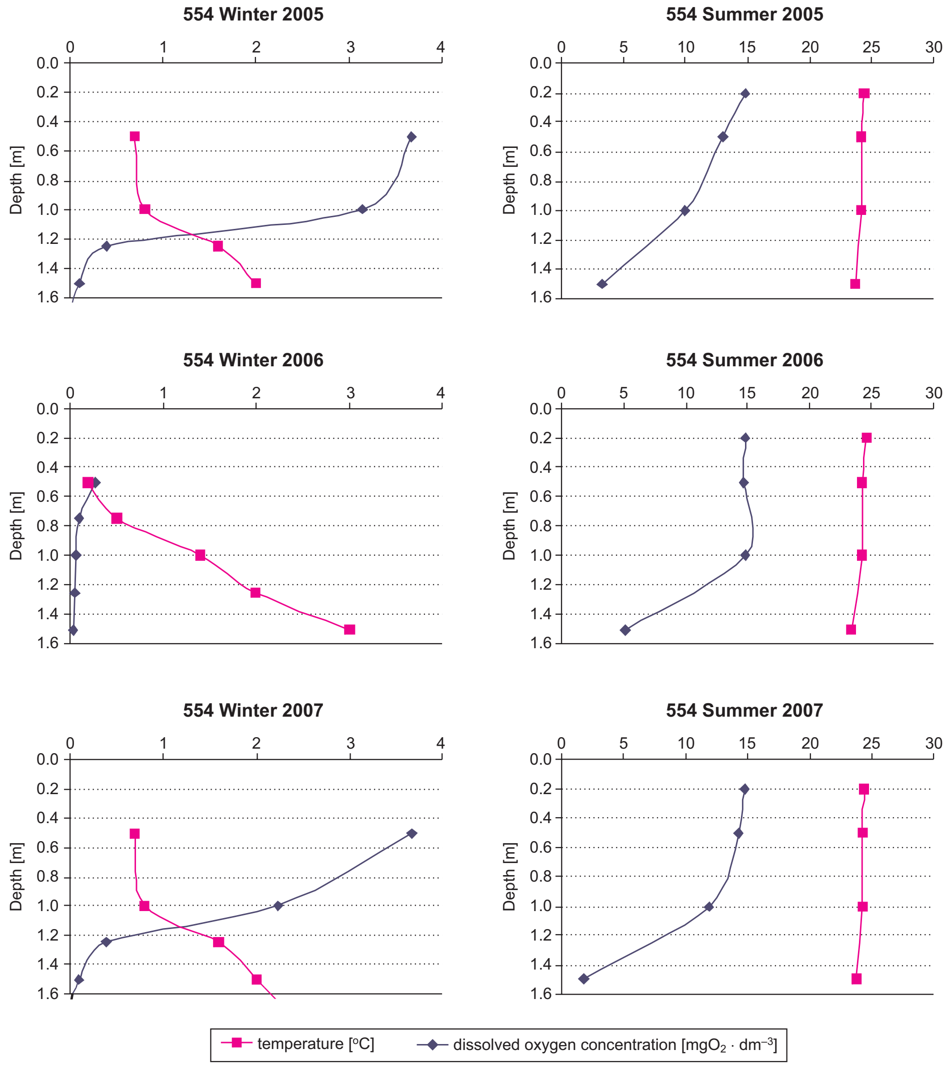

Fig. 2. Vertical distribution of temperature and dissolved oxygen concentrations ($\text{mgO}_2 \cdot \text{dm}^{-3}$) in the western part of Pilwa Bay during the winter and summer seasons of 2005–2007

for aquatic biocenoses are set at 2 $\text{mgO}_2\,.\,\text{dm}^3$ [4]. In the winter of 2006, the thickness of ice cover reached 60 cm, and oxygen could not be absorbed into water by direct diffusion from the atmosphere [5]. Photosynthesizing phytoplankton, mainly diatoms, may be a source of oxygen, but only under sufficient exposure to light. Light is able to penetrate the ice layer in the absence of snow cover, but the winter of 2006 was characterized by abundant snowfall. In the eastern part of the bay which is connected to the main lake basin, severe winter conditions did not decrease oxygen concentrations which reached 15.95 $\text{mgO}_2 \cdot \text{dm}^{-3}$ in the surface layer.

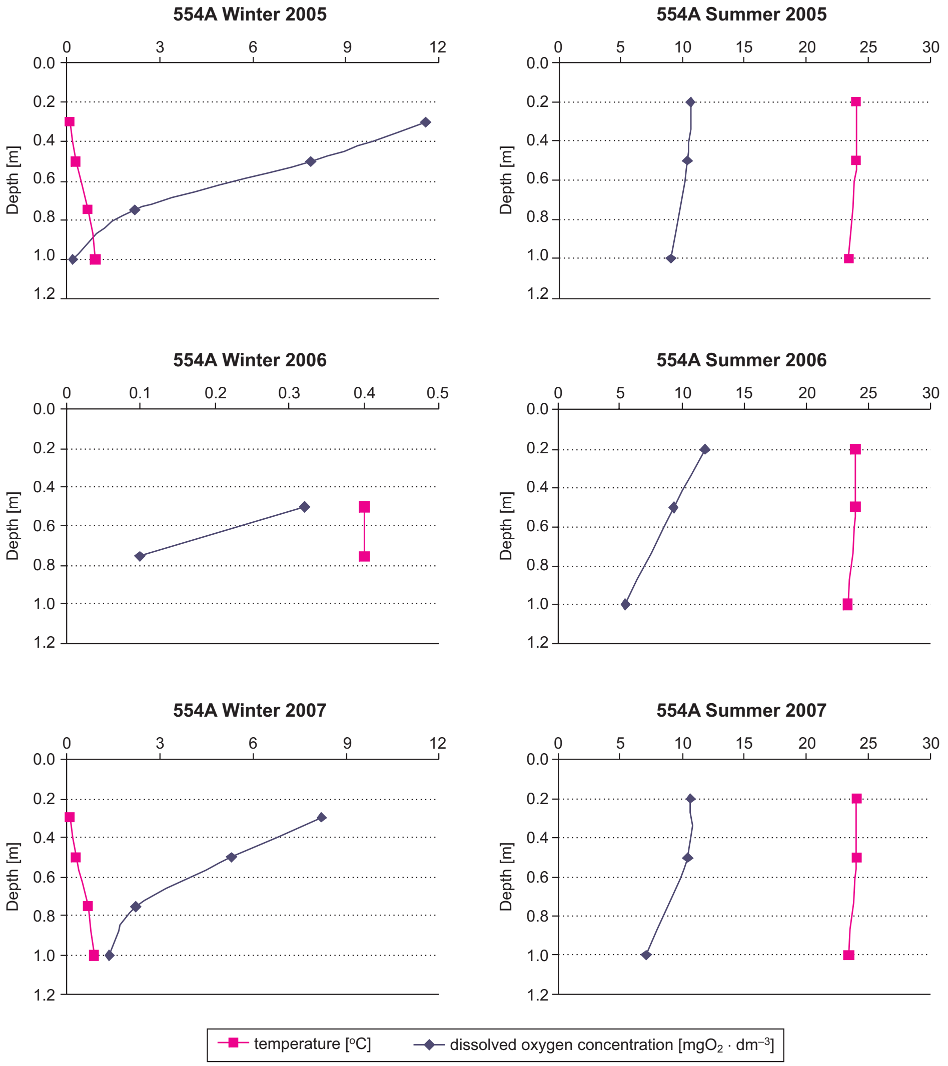

Fig. 3. Vertical distribution of temperature and dissolved oxygen concentrations (mgO$_2$ · dm^{-3}) in the central part of Pilwa Bay during the winter and summer seasons of 2005–2007

During summer stagnation, the bay was characterized by incomplete thermal and oxygen stratification which is typical of shallow water bodies. The temperature of the surface layer varied between 22.3 and 24.4 °C. An analysis of temperature and oxygen profiles revealed an insignificant temperature difference of approximately 1–2 °C between surface and bottom layers, which indicates that the examined bay was not characterized by a summer stratification pattern typical of deep water bodies. In the three-year period of the study, oxygen distribution patterns were correlated with temperature curves.

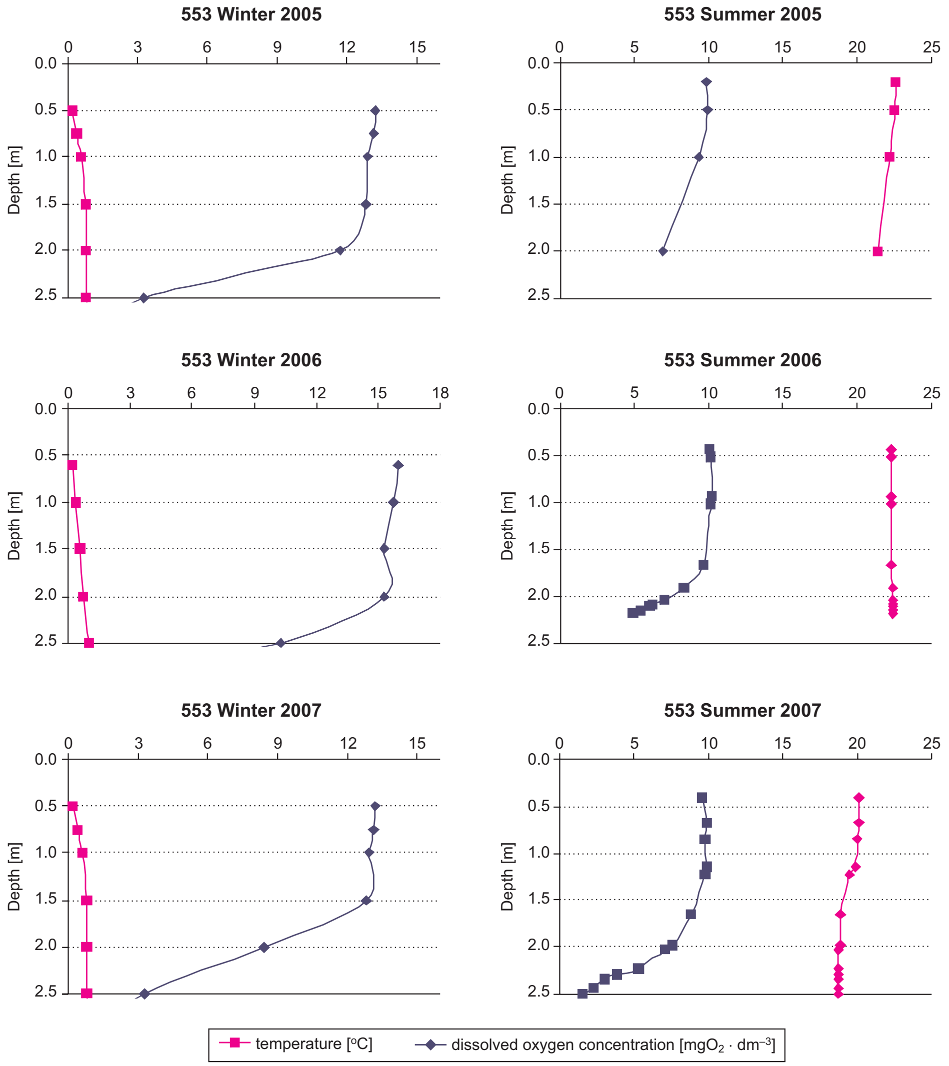

Fig. 4. Vertical distribution of temperature and dissolved oxygen concentrations ($mgO_2 \cdot dm^{-3}$) in the eastern part of Pilwa Bay during the winter and summer seasons of 2005–2007

Oxygen concentrations decreased with an increase in depth. A sudden drop in dissolved oxygen levels was noted in the depth range of 1 to 1.5 m. Shallow lakes have polymictic thermal-dynamic regime, and complete circulation of water contributes to uniform temperatures and free distribution of oxygen [6].

The electrolytic conductivity of the studied water body varied significantly between seasons (Table 1). In the winter, maximum electrolytic conductivity in the surface layer reached 810 $\mu S \cdot cm^{-1}$ in the central part (554A), and the lowest EC value of 370 $\mu S \cdot cm^{-1}$ was reported in the eastern section of the bay (553) which is connected to the main basin of Lake Dobskie. In the summer, the highest electrolytic conductivity of 476 $\mu S \cdot cm^{-1}$ was noted in the western part of the bay (554) which is supplied by two polluted watercourses. Elevated electrolytic conductivity values in runoffs from farmed areas were also reported by [7].

Table 1

Variation in the water parameters of Pilwa Bay in the years 2005–2007

Sampling site	Parameter	Season	Average from the years	Min	Max
Western part (554)	Conductivity [$\mu S \cdot cm^{-1}$]	Winter	577	437	716
		Summer	449	426	476
	pH	Winter	7.38	7.13	7.60
		Summer	8.53	7.95	8.80
	Oxygen saturation [%]	Winter	24	2	25
		Summer	150	119	178
	Transparency [m]	Summer – 0.3			
Central part (554A)	Conductivity [$\mu S \cdot cm^{-1}$]	Winter	713	463	810
		Summer	433	408	474
	pH	Winter	7.25	7.07	7.48
		Summer	8.08	8.12	8.44
	Oxygen saturation [%]	Winter	65	2	79
		Summer	113	106	126
	Transparency [m]	Summer – 1.0			
Eastern part connected to the main basin of Lake Dobskie (553)	Conductivity [$\mu S \cdot cm^{-1}$]	Winter	329	302	370
		Summer	327	316	359
	pH	Winter	8.39	8.24	8.52
		Summer	8.05	7.55	8.54
	Oxygen saturation [%]	Winter	97	100	109
		Summer	120	113	132
	Transparency [m]	Summer – 1.5			

The pH of the analyzed bay varied between 7.07 and 8.80. The maximum pH values were noted in the summer, due to the enhancing effects of photosynthesis. The minimum values were reported in the winter when organic matter decomposition lowered the pH of water.

The oxygen content of water fluctuates on a daily and seasonal basis. The highest oxygen saturation levels at 178 % were reported in the summer. According to [8], oxygen oversaturation may be encountered in eutrophic water bodies with high levels of primary production. The above phenomenon explains high oxygen concentrations in the summer when photosynthesis is intensified by extensive exposure to light and the growth of vascular plants, leading to the production of free oxygen in excess of 100 %.

Secchi disk measurements revealed the highest water transparency (up to 1.5 m) in the eastern section of the bay (553) which is connected to the main lake basin. The above results can be attributed to low algae content which is an important determinant of turbidity. The lowest levels of water transparency (0.3 m) were noted in the western part of the bay (554) due to the presence of cyanobacteria blooms [9].

Conclusions

1. During winter stagnation, the highest dissolved oxygen content in the Pilwa Bay was noted in the top water layer under ice cover, and oxygen concentrations varied widely between years.
2. Average dissolved oxygen concentrations were higher in the summer than in the winter. Oxygen solubility decreased with depth in the analyzed water body.
3. In the three-year period of the study, electric conductivity values were higher in the western part of the bay which is supplied with runoffs from semi-intensively farmed and intensively fertilized catchment areas than in the eastern section of the bay which is connected to the main basin of Lake Dobskie. Electric conductivity is a reliable indicator of water supply, circulation and dissolved organic matter concentrations, and it supports the identification of incidental events in catchment areas.

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ANALIZA WARUNKÓW TERMICZNO-TLENOWYCH WÓD W ZATOCE PILWA (JEZIORO DOBSKIE)

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Abstrakt: Badaniami objęto zatokę Pilwa jeziora Dobskiego położonego na obszarze mezoregionu Krainy Wielkich Jezior Mazurskich, w powiecie giżyckim. W niniejszej pracy przedstawiono warunki termiczno-tlenowe wód zatoki. Podczas trzyletnich prac badawczych (2005–2007) w okresie zimy i lata wykonano w zatoce (w części zachodniej, środkowej i wschodniej połączonej z głównym akwenem jeziora Dobskiego) pomiary rozkładu pionowego temperatury i tlenu rozpuszczonego. Pomiarów dokonano za pomocą sondy tlenowej z automatyczną kompensacją temperatury (WTW OXI Top OC 100).

W wyniku badań stwierdzono, że w czasie stagnacji zimowej największa zawartość tlenu rozpuszczonego znajdowała się w górnej warstwie pod powierzchnią lodu, a przebieg zmienności stężenia tlenu był bardzo zróżnicowany w poszczególnych latach. Z analizy profilu termiczno-tlenowego wynika, że istnieje niewielka różnica temperatur między powierzchnią lustra wody a dnem i wynosi ona około 1–2 °C, w związku z czym, nie można mówić o typowej stratyfikacji letniej, jaka występuje w akwenach głębokich.

Słowa kluczowe: profile termiczno-tlenowe, stratyfikacja termiczna, zatoka

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Andrzej SKWIERAWSKI[1]

THE USE OF THE INTEGRATED TROPHIC STATE INDEX IN EVALUATION OF THE RESTORED SHALLOW WATER BODIES

ZASTOSOWANIE INTEGRALNEGO WSKAŹNIKA STANU TROFICZNEGO DO OCENY ODTWORZONYCH PŁYTKICH ZBIORNIKÓW

Abstract: The aim of this study was to determine the trophic status of five restored shallow lakes from a group of 30 water bodies in the Olsztyn Lakeland, which were dried in the 19th century as part of a land reclamation program. The effectiveness of the Integrated Trophic State Index (ITS) in the evaluation process was analyzed. ITS is a relatively new method for diagnosing eutrophication intensity. It analyzes the balance between production processes and organic matter decomposition through simultaneous measurements of oxygen saturation and pH of water. ITS is a versatile tool which can be applied in various types of water bodies. In this study, it was used to evaluate shallow water bodies characterized by excessive phosphorus loads and susceptibility to blue-green algal blooms in summer.

During a three-year study carried out in 2010–2012, significant correlations were observed between %O_2 and pH, which is a basic prerequisite for applying the ITS method. In the analyzed water bodies, correlation coefficients were determined in the range of $r = 0.68–0.83$. ITS values varied in successive years ITS (from 7.73 to 8.67), ranging from eutrophy to hypertrophy. Most ITS scores were consistent with the values of Carlson's TSI, which indicates that used integrated trophic state index, based on the values of water pH and oxygen saturation, accurately reflect the ecological status of degraded water bodies.

Keywords: trophic state, Carlson's TSI, Integrated Trophic State Index (ITS), restored lakes, eutrophication

The trophic state is an indicator of the degree of transformation and ecological disruption of water bodies. Various methods for evaluating the trophic state have been proposed based on different criteria, such as nutrient supply, primary production levels or changes observed in trophic structure in comparison with undisturbed ecosystems [1–5]. Commonly used models evaluate the concentrations of primary biogenic compounds (nitrogen and phosphorus) and phytoplankton characteristics (concentrations of chlorophyll a and Secchi disc visibility). Those parameters are taken into account in the most popular models: the Vollenweider model [6, 7] and Carlson's Trophic State Index [8].

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In 1995, Neverova-Dziopak proposed the Integrated Trophic State Index (ITS) as a new method for evaluating primary production levels in water bodies [3]. Unlike conventional evaluation tools, this method analyzes the balance between primary production and organic matter decomposition by measuring dissolved oxygen levels and pH of water. A water body's trophic status is evaluated by diagnosing changes in an aquatic ecosystem caused by intensified primary production [3, 4]. ITS is a versatile tool which can be applied in various types of water bodies. Its main advantage is the ease of obtaining output data for trophic state assessments: only two indicators (% oxygen saturation and pH of water) which are measured during standard water quality inspections are required. ITS significantly simplifies the evaluation process. Every new method should be tested under various conditions to analyze its suitability and reliability. To date, ITS has been rarely used by researchers in evaluations of various water ecosystems [3, 9–11]. In this study, the discussed method was used to assess degraded water bodies which generally score poorly when conventional evaluation tools are applied.

The objective of this study was to evaluate the trophic status of restored shallow water bodies which constitute a rare and poorly investigated category of aquatic ecosystems. The second objective was to test the effectiveness of ITS in evaluations of eutrophic water bodies by comparing the obtained results with the values of Carlson's TSI.

Materials and methods

The study was carried out on five restored shallow lakes from a group of 30 water bodies in the Olsztyn Lakeland which had been dried in the 19th century as part of a land reclamation program and were restored or allowed to refill naturally [12]. The analyzed water bodies were restored around 1980, excluding Lake Gasiorowskie, which was refilled in the mid 1960s. All lakes are characterized by a small surface area, a low maximum depth and the predominance of farmland in their catchment areas (Table 1).

Table 1

Characteristics of the surveyed water bodies (based on own measurements)

Lake designation	Geographical location	Area [ha]		Max depth [m]	Catchment basin usage* [%]			
		Lake	Catchment basin		AL	BA	F	W
Nowe Wloki – southern section	53°54′13″ N 20°31′25″ E	15.2	173	2.6	88.0	0.3	2.9	8.8
Nowe Wloki – northern section	53°53′58″ N 20°31′42″ E	4.6	202	2.7	80.2	8.6	9.6	1.6
Setal Pond	53°54′14″ N 20°28′57″ E	3.7	103	1.5	83.9	12.2	0.0	3.9
Dobrazek	53°49′50″ N 20°47′40″ E	9.3	105	2.5	93.0	1.2	5.2	0.5
Gasiorowskie	53°43′13″ N 20°48′53″ E	6.9	34	4.0	55.8	11.8	32.4	0.0

* Land use designations: AL – agricultural land, BA – built-up area, F – forest, W – surface waters and wetlands.

Lake Nowe Wloki and Setal Pond were characterized by stable phytoplankton communities with a predominance of Cyanobacteria. Weakly developed submerged macrophytes and moderate phytoplankton blooms were observed in Lake Dobrazek. Lake Gasiorowskie was classified as a pure water system where macrophytes, mostly floating-leaf plants (*Nymphaea alba* and *Nuphar lutea*), were the most important primary producers. Progressive disappearance of vascular plants was observed in the above lake.

The study was carried out from 8th November 2010 to 10th September 2012. A total of 23 water samples were collected from each of the five analyzed lakes, at about 6 week intervals throughout the whole period of observations. The indicators for calculating ITS were measured locally with the use of the YSI 6600 multiparameter sonde. The results were calculated separately for every lake based on data from year-long measurements with the use of the following formula [3]:

$$\mathrm{ITS} = \Sigma\ \mathrm{pH}_i\ /\ n + a\,(100 - \Sigma\ [\mathrm{O}_2\%]\ /\ n)$$

where: pH_i – water pH,
$[\mathrm{O}_2\%]$ – oxygen saturation of water,
a – coefficient of regression between pH and $\%\mathrm{O}_2$,
n – number of measurements.

Comparative data for determinations for Carlson's TSI were obtained simultaneously with measurements of oxygen saturation and pH of water. Only the measurements performed in the growing seasons of each analyzed year (May–September) were used to calculate Carlson's TSI. Partial TSI scores were determined based on phosphorus levels ($\mathrm{TSI}_{\mathrm{TP}}$), concentrations of chlorophyll a ($\mathrm{TSI}_{\mathrm{Chl}}$) and Secchi disc visibility ($\mathrm{TSI}_{\mathrm{SD}}$) with the use of the following formulas [7].

$$\mathrm{TSI}_{\mathrm{TP}} = 14.42 \cdot \ln(\mathrm{TP}) + 4.15$$

$$\mathrm{TSI}_{\mathrm{Chl}} = 9.81 \cdot \ln(\mathrm{Chl}) + 30.6$$

$$\mathrm{TSI}_{\mathrm{SD}} = 60 - 14.41 \cdot \ln(\mathrm{SD})$$

where: TP – phosphorus levels $[\mu\mathrm{g} \cdot \mathrm{dm}^{-3}]$,
Chl – concentrations of chlorophyll *a* $[\mu\mathrm{g} \cdot \mathrm{dm}^{-3}]$,
SD – Secchi disc visibility [m].

Phosphorus levels were determined in a laboratory with the use of ammonium molybdate and tin(II) chloride after sample mineralization. Chlorophyll concentrations were measured with the YSI 6600 sonde, and Secchi disc visibility was determined during lake measurements with the involvement of a standard black and white disc with the diameter of 20 cm. The data were processed in line with the principles applicable to ITS and Carlson's TSI. The results were verified statistically in the Statistica 10 PL application.

Results and discussion

Carlson's TSI revealed variations in the trophic status of the analyzed water bodies which ranged from moderate to high nutrient levels (Table 2). Regardless of the final result, visible disproportions in correlations between $TSI_{TP} > TSI_{Chl} \approx TSI_{SD}$ were observed in all water bodies. This correlation is characteristic of water bodies with a predominance of phytoplankton where a small euphotic zone determines the intensity of primary production. The above is triggered by the accumulation of unused phosphorus reserves in water in both mineral form and in the form of dead organic matter. The results of other studies indicate that restored shallow lakes are generally characterized by excessive phosphorus loads [13, 14]. Phosphorus ceases to limit primary production, and high levels of that element contribute to negative results of trophic state assessments performed with methods based on phosphorus concentrations. The resulting evaluations are less reliable and their results are overestimated because such methods rely on the assumption that productivity levels can be regulated by periodic phosphorus deficiencies. In water bodies with excessive nutrient loads, phosphorus plays the role of a reserve substrate in the ecosystem. In polymictic lakes, the above contributes to the preservation of high phytoplankton levels and turbid-water conditions. In such lakes, powerful mechanisms prevent the recovery of pure water conditions with a predominance of submerged vegetation which enhance the lake's general usability classification and ecological parameters [15, 16]. Such a state was also observed in the studied group of lakes, including the pure-water Lake Gasiorowskie. High values of TSI_{TP} were reported in all of the analyzed water bodies (Table 2).

Table 2

The results of trophic state assessment based on the values of Carlson's TSI in the studied lakes in 2010–2012

Lake	Year	TSI partial results			Results	
		TSI_{TP}	TSI_{Chl}	TSI_{SD}	TSI	State*
Nowe Wloki – southern section	2010	72.4	57.1	68.0	65.9	**E**
	2011	78.3	64.6	69.6	70.8	**H**
	2012	74.7	62.8	68.4	68.7	**E**
Nowe Wloki – northern section	2010	74.5	58.7	64.8	66.0	**E**
	2011	81.5	62.6	66.7	70.3	**H**
	2012	79.8	66.7	67.0	71.2	**H**
Setal Pond	2010	91.8	68.9	65.3	75.3	**H**
	2011	87.6	68.4	72.3	76.1	**H**
	2012	83.5	65.2	69.7	72.8	**H**
Dobrazek	2010	72.4	57.6	63.0	64.3	**E**
	2011	71.2	63.7	59.7	64.9	**E**
	2012	74.6	60.7	61.1	65.5	**E**
Gasiorowskie	2010	71.7	50.9	51.2	57.9	**E**
	2011	57.8	54.4	50.3	54.2	**E**
	2012	61.0	51.7	50.9	54.5	**E**

* Trophic state categories: E – eutrophic; H – hypertrophic.

The ITS method can be applied to water bodies characterized by significant correlations between oxygen saturation and pH of water. The data collected in the entire group of evaluated lakes (n = 116) confirmed the presence of such relationships, and the coefficient of correlation was determined at r = 0.743 (Fig. 1). In most water bodies, oxygen saturation was determined at 80–120 % and pH at 7.5–9.0, which is typical of lakes with moderate and high nutrient levels. Considerable statistical dispersion was observed – the lowest values were recorded in winter (oxygen saturation < 40 %, relatively low pH), whereas Setal Pond was characterized by 222.4 % oxygen saturation of pH of 10.46 in the summer of 2012. Those extreme results did not, however, diverge from the regression curve (Fig. 1).

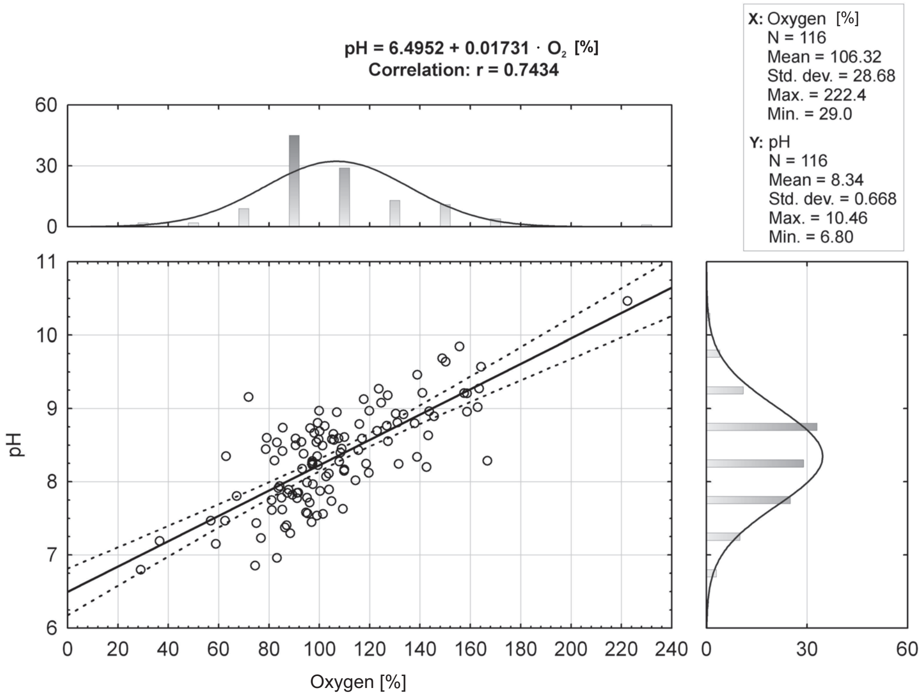

Fig. 1. Correlations between oxygen saturation and pH of water based on data collected from the analyzed water bodies, shows that changes of two groups of output parameters were interconnected

The evaluations of trophic status based on ITS values were similar to the results produced by Carlson’s TSI method. In nine out of 15 analyzed water bodies, ITS scores were identical to the results of Carlson’s TSI (Tables 2 and 3). The remaining results differed by one trophic class, and lower trophic states were denoted by ITS values in all cases. ITS scores were most correlated with partial TSI values based on the concentrations of chlorophyll a (TSI_{Chl}), an indicator of phytoplankton biomass. In shallow lakes, chlorophyll levels are the most robust indicator of intensive primary production because Secchi disc visibility can be limited by sediment resuspension which lowers water transparency and increases phosphorus concentrations in water [17].

ITS and TSI values diverged most significantly in 2010 which was characterized by a long winter and high precipitation levels in early summer. The above conditions contributed to lower pH of water which decreased ITS values in comparison with the remaining years of the experiment and TSI scores.

Table 3

The results of trophic state assessment based on ITS values in the studied lakes in 2010–2012

Lake	Year	Correlation coefficient	Indicators to calculate ITS value		Regression coefficient *a*	Results	
			Σ pH$_i$/*n*	Σ [O$_2$%] /*n*		ITS	State*
Nowe Wloki – southern section	2010	0.936	7.948	99.82	0.01685	7.95	**M**
	2011	0.837	8.499	112.04	0.01764	8.29	**E**
	2012	0.839	8.813	114.65	0.01724	8.56	**E**
Nowe Wloki – northern section	2010	0.764	7.915	96.03	0.02605	8.02	**E**
	2011	0.644	8.383	112.11	0.01500	8.20	**E**
	2012	0.831	8.818	117.31	0.01149	8.62	**H**
Setal Pond	2010	0.356	7.921	88.67	0.00899	8.02	**E**
	2011	0.854	8.576	113.59	0.01537	8.37	**E**
	2012	0.937	9.051	126.45	0.01370	8.69	**H**
Dobrazek	2010	0.801	7.944	108.29	0.02599	7.73	**M**
	2011	0.706	8.218	102.35	0.01754	8.18	**E**
	2012	0.690	8.707	109.98	0.01379	8.57	**E**
Gasiorowskie	2010	0.750	7.754	91.37	0.03519	8.06	**E**
	2011	0.693	8.157	96.82	0.01123	8.19	**E**
	2012	0.778	8.349	98.51	0.01834	8.38	**E**

* Trophic state categories: M – mesotrophic; E – eutrophic; H – hypertrophic.

No significant correlations were reported between ITS and TSI results (r = 0.240, Table 3). ITS scores were not correlated with any input indicators used in the TSI method (phosphorus and chlorophyll concentrations, Secchi disc visibility). ITS values reflect the intensity of primary production and organic matter decomposition which are indicative of the lake's ecological status. Methods that rely on the concentrations of biogenic compounds in water investigate lakes' ability to produce organic matter which can be limited by various factors (light availability, accumulation of toxic substances), preventing producers from

Lake Dobrazek was an exception in the analyzed group of water bodies. Significant changes in its catchment area were observed during the period of the study. The southern part of the catchment was completely transformed due to a road reconstruction project. After the project's completion in 2012, the main pipe of the road drainage system was emptied into the lake, contributing a new source of pollution. TSI values indicate that the lake did not respond to the above changes within the standard range of trophic indicators (Table 3), whereas ITS scores based on oxygen saturation and pH of water increased significantly in comparison with 2010 when the lake was classified as eutrophic/mesotrophic (Table 4). This suggests that the ITS method provided a quicker response to increased external pressure. Further work is, however, needed to validate this hypothesis.

Table 4

Pearson's matrix of correlations between TSI / ITS values and respective index components for the group of investigated water bodies in different years of the study (values in bold are statistically significant at $p < 0.05$)

Variable	ITS	TSI	Chl_a	SD	P	pH
ITS	—					
TSI	0.240	—				
Chl_a	0.334	**0.897**	—			
SD	–0.157	**–0.911**	**0.684**	—		
P	0.092	**0.843**	**0.878**	**–0.581**	—	
pH	**0.927**	0.407	0.426	–0.394	0.149	—
O_2	**0.668**	0.498	0.375	**–0.577**	0.126	**0.878**

Explanations: Chl_a – chlorophyll a; SD – Secchi disk depth; P – concentration of total phosphorus; O_2 – oxygen saturation.

An absence of correlations between phosphorus concentrations and ITS scores (Table 4) confirms that in lake ecosystems with excessive phosphorus loads, the discussed element, which controls primary production in lakes with low and moderate nutrient levels, ceases to regulate productivity [18, 19]. In lakes characterized by stable turbid-water states, the key parameter is light availability [20, 21]. In evaluations of trophic status, a narrow euphotic zone is reflected by the results of Secchi disc visibility tests. Excess phosphorus concentrations cease to determine a lake's ability to fulfill ecological and economic functions. In this case, it is no longer significant whether primary production limits are exceeded three- or 10-fold because a lake's ecological condition can be similar in both scenarios. When phosphorus loads are considerably exceeded, TSI values and the trophic status determined by the diagnostic model will point to a higher level of degradation. This has important practical implications and is of a high informative value because positive results of protective and reclamation efforts in lakes are more difficult to achieve when phosphorus loads are very high.

Conclusions

1. The evaluated five restored water bodies were characterized by high nutrient loads, in particular excessive phosphorus concentrations. During the experiment, TSI values for phosphorus were significantly higher than TSI_{Chl} and TSI_{SD}, which indicates that the euphotic zone was the key factor limiting primary production. The above correlation is characteristic of lakes with a stable turbid-water state and a predominance of Cyanobacteria.

2. In Lake Gasiorowskie, which was restored earlier than the other studied water bodies and was characterized by lower phytoplankton abundance and a high share of vascular plants, less pronounced differences were reported between phosphorus and

chlorophyll concentrations and Secchi disc visibility. The results of TSI index for this lake were the most advantageous compared to other studied sites.

3. The integrated trophic state index (ITS) revealed relatively high nutrient loads in the studied water bodies. In most lakes, ITS scores were largely consistent with TSI values. The obtained data indicate that ITS is a synthetic indicator that accounts for all functional aspects of an aquatic ecosystem. ITS values are largely independent of phosphorus loads, whereas the TSI method assigns a higher trophic class to lakes with excess phosphorus concentrations.

Acknowledgements

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ZASTOSOWANIE INTEGRALNEGO WSKAŹNIKA STANU TROFICZNEGO DO OCENY ODTWORZONYCH PŁYTKICH ZBIORNIKÓW

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Abstrakt: W pracy podjęto próbę oceny stanu troficznego pięciu płytkich zbiorników, należących do grupy około 30 obiektów Pojezierza Olsztyńskiego, współcześnie odtworzonych po osuszeniu dokonanym w XIX w. W szczególności przeanalizowano możliwość zastosowania integralnego wskaźnika troficzności (*Index of Trophical State* – ITS). Wskaźnik ten jest stosunkowo nową metodą diagnozy nasilenia procesu eutrofizacji. Bazuje na ocenie równowagi procesów produkcji i rozkładu materii organicznej, którą określa się poprzez symultaniczny pomiar nasycenia wody tlenem i odczynu. Metoda ta jest przedstawiana jako uniwersalna, mająca zastosowanie w różnych typach wód. W niniejszej pracy wykorzystano ją do oceny zbiorników płytkich, cechujących się dużym nadmiarem fosforu w obiegu i podatnych na zakwity sinic w sezonie letnim (często bardzo intensywne).

Badania w przekroju 3 lat (2010–2012) wykazały istotną statystycznie korelację pomiędzy $\%O_2$ i pH, co jest podstawowym wymogiem możliwości zastosowania wskaźnika ITS. Współczynniki korelacji dla poszczególnych obiektów wodnych wynosiły r = 0,68–0,83. Wyniki oceny stanu w kolejnych latach zmieniały się w zakresie od eutrofii do wartości wykraczających poza granicę tego stanu (ITS od 7,73 do 8,67). Uzyskane wyniki w większości przypadków były zgodne z rezultatami oceny powszechnie stosowanej metody TSI Carlsona, co wskazuje, że również w zdegradowanych zbiornikach relacja pH-O_2 odzwierciedla ich stan ekologiczny.

Słowa kluczowe: stan troficzny, TSI Carlsona, wskaźnik ITS, odtworzone jeziora, eutrofizacja

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NANOFILTRATION OF FERMENTATION SOLUTIONS – UNFAVOURABLE PHENOMENA AND MEMBRANE CLEANING

NANOFILTRACJA ROZTWORÓW FERMENTACYJNYCH – ZJAWISKA NIEKORZYSTNE ORAZ CZYSZCZENIE MEMBRAN

Abstract: The intensity of unfavourable phenomena occurring in the nanofiltration process of fermentation solutions, and the possibility of cleaning the membranes after this process were studied. The experiment was carried out using a tubular module equipped with the AFC-30 membrane. The filtration process was carried out at a transmembrane pressure of 2.0 MPa, linear velocity of the feed of 3.4 m/s and the temperature of the feed equal to 20 °C. Hydraulic performance of the membrane was tested both during the filtration of model and real solutions. The conditions for efficient cleaning of fouled surfaces of the membranes by using different chemical reagents were determined. It was also attempted to rinse the membrane with clean water. A preliminary study was performed to determine the transport and separation characteristics of the AFC-30 membrane for deionized water and salt solutions of NaCl and $MgSO_4$ representing mono- and divalent ions, respectively. In this case, the membrane was tested under varying transmembrane pressure in the range of 1.0 to 2.0 MPa.

Keywords: nanofiltration, fermentation solutions, decrease of hydraulic capacity of membrane, membrane surface cleaning

Membrane techniques are used, among others, as a separation tool in separation processes used for technological and waste streams occurring in the liquid or gas phase [1]. The use of pressure-driven membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis, has become increasingly common in the case of liquid streams. Those processes have been applied in order to isolate the individual components present in the form of suspensions, colloids or true solution [1–2]. The characteristics of the pressure-driven membrane processes are presented in

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Table 1. The membranes are characterized by increasingly smaller pore size and smaller volumetric flux of permeate, depending on which process is concerned: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO). Theoretically, the most dense membrane are only water-permeable and are used for the reverse osmosis process. Nanofiltration membranes, on the other hand, allow for the separation of ions of different valency and separation of organic substances, and ultrafiltration membranes retain fine suspensions, colloids, bacteria and viruses. Microfiltration membranes, which have the largest pores, permit separation of suspended microparticles. Due to the physical structure of membranes their hydraulic resistance increases hence correspondingly higher driving pressure is applied.

Table 1

Comparison of pressure-driven membrane processes [1]

Process	Transmembrane pressure [MPa]	Volumetric permeate flux [$m^3/m^2 \cdot s \cdot MPa$]
Microfiltration (MF)	0.01–0.2	$> 13.89 \cdot 10^{-5}$
Ultrafiltration (UF)	0.1–0.5	$2.78 \cdot 10^{-5}$–$13.89 \cdot 10^{-5}$
Nanofiltration (NF)	0.5–2.0	$0.39 \cdot 10^{-5}$–$3.33 \cdot 10^{-5}$
Reverse osmosis (RO)	1.0–10.0	$0.01 \cdot 10^{-5}$–$0.39 \cdot 10^{-5}$

The disadvantages associated with the membrane processes primarily concern the reduction of the hydraulic performance of membranes caused by adverse side effects of membrane filtration, this is, concentration polarization, formation of a gel layer on the membrane surface, the accumulation of impurities on the membrane surface or within the pores (fouling), and precipitation of sparingly soluble salts forming inorganic deposits (scaling) [3–8]. These phenomena occur simultaneously, and their negative effects are cumulative. As a result, a gradual decrease in the volumetric flux of permeate occurs during the operation of a membrane installation. The phenomenon of concentration polarization causes the formation of a boundary layer (termed as polarization layer) occurring in the immediate vicinity of the membrane and characterized by the solute concentration exceeding its mean concentration in the feed [1]. Concentration polarization effects are the most important in the processes of reverse osmosis and nanofiltration, and occur to a lesser extent in the process of microfiltration. The solid or thixotropic gels are formed when the solubility of a substance in the polarizing layer is exceeded [9]. The gel layer which exists between the membrane and the solution forms a secondary membrane. A phenomenon of precipitation of sparingly soluble salts (scaling), particularly calcium sulfate and calcium carbonate, may occur within the polarization layer or the concentrated solution on the membrane in the processes of reverse osmosis and nanofiltration [10]. Scaling of the membrane is therefore an adverse effect of the concentration polarization. The phenomenon of fouling occurs in the case of membrane processes, in which porous membranes are used (as in microfiltration and ultrafiltration), but also in the processes of reverse osmosis and nanofiltration, which require the pre-treatment of the feed [11]. Fouling can occur as a reversible or irreversible process. The former case is when the deposits retained on a membrane can be completely removed enabling full restoration of the initial performance of a membrane. The process in which membrane fouling is caused by microorganisms is referred to as biofouling.

The adverse effects of all the above-discussed phenomena can be limited by several methods [1, 12]:

1) pre-treatment of the feed,
2) modification of the properties of the membrane,
3) ensuring optimal operational parameters of membrane installation,
4) cleaning the membranes.

The required treatment degree of the feed depends on the type of membrane process [1]. For example, in order to reduce fouling it is necessary to remove suspended solids, colloids, soluble macromolecules and microorganisms [11]. To this end, the following processes can be used: filtration, coagulation, disinfection, and adsorption on activated carbon. Modification of membranes allows for change of those properties that have major impact on fouling [1]. Those changes can be achieved by the use of small currents, the chemical adsorption of ionic substances, or by binding enzymes on the membrane surface. The optimization of operating parameters of a membrane process consists in, for example, selecting the appropriate hydrophobic of hydrophilic membrane, its pore size, and transmembrane pressure [10]. Since the application of the above-discussed solutions does not completely eliminate membrane blocking it is necessary to clean the membranes periodically. It can be carried out by chemical, hydraulic or mechanical methods [12]. Hydraulic cleaning involves rinsing the membrane with water and air or backwashing under reduced pressure. For chemical cleaning, depending on the composition of the deposited impurities, suitable chemical reagents are used, this is, phosphoric acid or citric acid, sodium hydroxide, anionic or nonionic detergents and complexing agents.

The aim of this study was to evaluate the intensity of adverse phenomena and the possibility of cleaning membranes used for nanofiltration of fermentation solution. Transport and separation properties of a nanofiltration membrane (AFC-30) were also determined. Separation properties of the membrane with respect to the components of the filtered fermentation solutions were not studied.

Materials and methods

Nanofiltration was carried out using a system with a cross-flow module equipped with a tubular membrane AFC-30 by company PCI Membrane System, Inc. (USA). The characteristics of the membrane are shown in Table 2.

Table 2

Characteristic of the AFC-30 membrane

Membrane	Material	Max pH range	Max pressure [MPa]	Max temp. [^oC]	Molecular weight cut-off [Da]	Removal of $CaCl_2$ [%]
AFC-30	composite (active layer-polyamide)	1.5–9.5	6.0	60	200	75

The transport and separation characteristics of the membrane were determined in the preliminary study using deionized water and salt solutions of sodium chloride NaCl and magnesium sulfate $MgSO_4$ (concentration 1 g/dm^3) representing mono- and divalent ions, respectively. These studies were performed under varying conditions of trans-membrane pressure in the range of 1.0 to 2.0 MPa.

The effectiveness of filtration was assessed by determination the volumetric and relative permeate fluxes (J_w – for deionized water, J_v – for the model and real fermentation solutions (1) and α – relative permeability of membrane (2), Table 3). The concentration of the ions were assayed in the solutions (feed) and that purified with membrane techniques (permeate), which then formed the basis for calculating their retention coefficient R (3).

Table 3

Equations used to evaluate membrane properties and removal efficiencies

Parameter	Equation
Volumetric permeate flux, J_v (J_w) [m^3/m^2 · s]	$J_v(J_w) = \frac{V}{F \cdot t}$ (1)
Relative permeability of membrane, α	$\alpha = \frac{J_v}{J_w}$ (2)
Retention coefficient, R [%]	$R = \left(1 - \frac{C_p}{C_t}\right) \cdot 100$ (3)

V – volume [dm^3], F – membrane area [m^2], t – filtration time [s], C – concentrations [g/dm^3], f – feed, p – permeate.

Two types of solutions were used in the main part of the experiment. These solutions were: a model solution based on deionized water containing broth in a concentration of 1 g/dm^3 (MRS type, BTL Poland), and the real fermentation solution, which had previously been concentrated by ultrafiltration using a ceramic tubular membrane with a molecular weight cut-off 8000 Da. The main components of a fermentation solution were: glycerol, 1,3-propanediol, citric acid, lactic acid and acetic acid at a concentration of 13.49 g/dm^3, 2.44 g/dm^3, 2.40 g/dm^3, 0.74 g/dm^3 and 0.52 g/dm^3, respectively. Small amounts of mineral salts such as K_2HPO_4, KH_2PO_4, $(NH_4)_2SO_4$, $MgSO_4 \cdot 7\,H_2O$, $CaCl_2$ and $CoCl_2$ were also present in the test solution.

The membrane cleaning was carried out as a multi-stage process. For this purpose, the membranes were rinsed with deionized water (stage I) and were also cleaned chemically using 1 % basic solution of NaOH (stage II and IV) as well as 0.5 % aqueous solution of H_3PO_4 (stage III). The efficiency of membrane cleaning was determined based on the relative permeability of membrane α, which is the ratio of specific streams of deionized water before and after the regeneration process (mean value determined for the tested filtration cycles).

Results and discussion

The main parameter, which describes the transport properties of the membrane is the hydraulic performance determined by the volumetric flow of permeate (J_w). Figure 1 shows the dependence of the volumetric flow of deionized water on the process transmembrane pressure for the tested AFC-30 nanofiltration membrane. The deionized water flux increases with increasing transmembrane pressure, but is dependent to a small extent on the duration of the process (Fig. 2). The values of the tested parameter were in the classic range specified for nanofiltration membranes (Table 1).

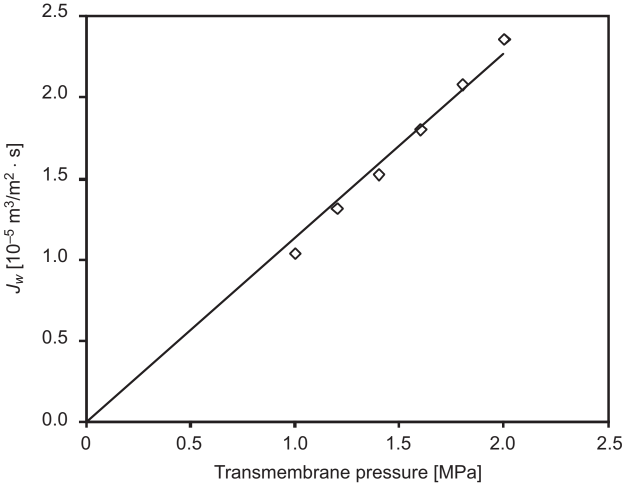

Fig. 1. Relationship between volume flux of deionized water and transmembrane pressure

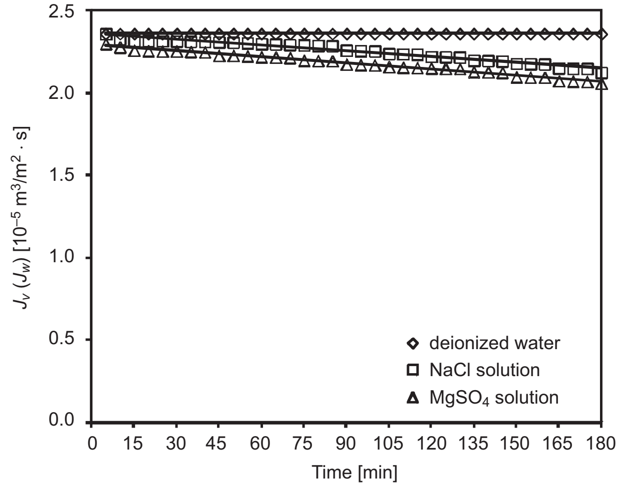

Fig. 2. Volumetric permeate flux on time during filtrations of deionized water and salt solutions (transmembrane pressure 2.0 MPa)

The retention factor for sodium chloride and magnesium sulfate (representing mono- and divalent ions, respectively) determines the separation properties of the nanofiltration membranes. For the AFC-30 membrane the retention coefficient of sodium chloride and magnesium sulfate was medium and high (approx. 58 and 83 %), respectively (Table 4).

Table 4

Volumetric permeate flux, relative permeability of the membrane and retention coefficient of NaCl and $MgSO_4$

Salt	Volumetric flux of deionized water $J_w \cdot 10^{-5}$ m^3/m$^2 \cdot$ s	Relative permeability of the membrane α [-]	Salt retention [%]
NaCl	2.36	0.95	58.4
$MgSO_4$		0.92	83.1

The obtained value of the salt retention coefficients, especially of sodium chloride, is not typical for nanofiltration membranes. The effect of the divalent ion separation is usually approx. three-fold higher than the effect observed for monovalent ions [13]. On this basis, it can be assumed that the tested nanofiltration membrane has separation properties similar to the membranes used in reverse osmosis. The salt retention depends on the process transmembrane pressure (Fig. 3). The retention of sodium chloride and magnesium sulfate is increasing with the increase in transmembrane pressure. The reason for this phenomenon is complex and results, among others, from the reduced concentration of salt at the membrane surface due to the increased feed flux [14].

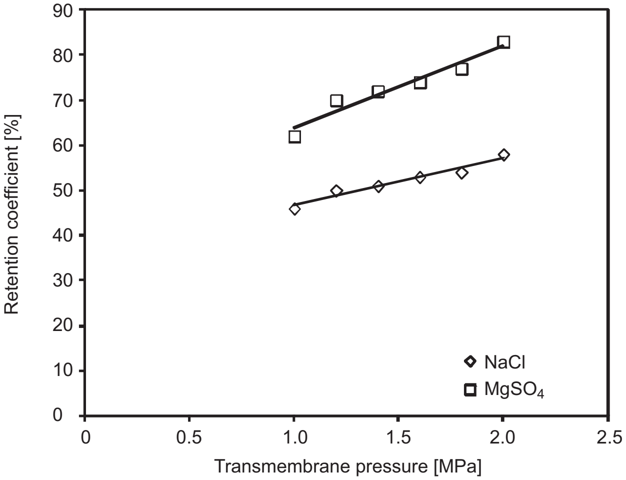

Fig. 3. Relationship between retention coefficient of NaCl or $MgSO_4$ and transmembrane pressure

During the filtration of salt solutions a decrease of volumetric permeate flux was observed (Fig. 2). The relative permeability of membrane α was respectively 0.95 for the filtration of NaCl solution and 0.92 for the filtration of $MgSO_4$ solution. This can be confirmed by the occurrence of adverse phenomena during the membrane filtration such as the concentration polarization.

Figure 4 shows the changes in hydraulic performance of the membrane during nanofiltration of the test solutions (a – model solution, b – real solution), and during the process of cleaning the membrane. In contrast, Figure 5 shows the average values of the relative permeability of membrane α, which characterize the respective filtrations.

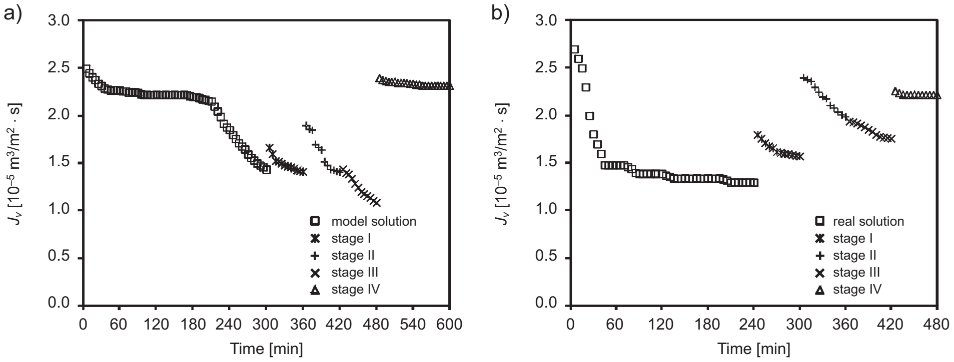

Fig. 4. Effect of type of solution (a – model; b – real) and cleaning process on hydraulic membrane capacity

The study indicated that nanofiltration of the real fermentation solution was characterized by rapid decrease of the hydraulic performance of the membrane in the first hour of filtration. In the case of filtration of the model solution similar phenomenon occurred in the fourth hour of the process. Based on these observations it appears that in the case of filtration of the real fermentation solution, fouling was found to be the predominant process among the adverse effects that accompany membrane filtration,

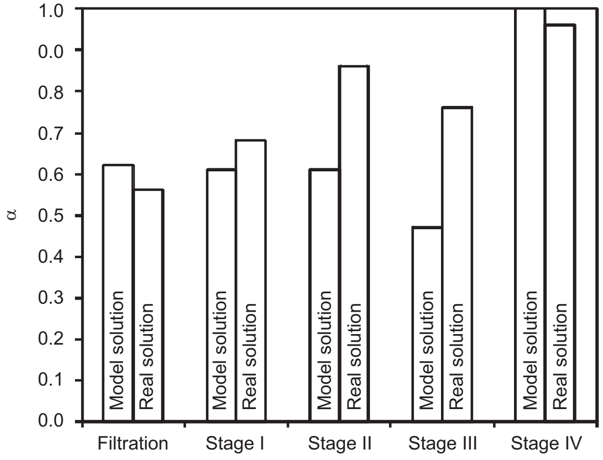

Fig. 5. Comparison of the relative volumetric permeate flux α in nanofiltration of investigated solutions and after cleaning process

since it usually occurs in the initial filtration step [3]. In the case of filtering the model solution a large amount of organic matter could have been rapidly retained on the membrane surface, probably due to the increase in the concentration of pollutants in the near-membrane layer (and concentration polarization phenomenon occurring simultaneously), which resulted in sharp reduction of the membrane hydraulic capacity. However, due to putrescibility of the broth, which is the basic component of the feed, the biofouling of the membrane cannot be ruled out [15, 16]. The value of the relative permeability of the membrane depended on the type of the feed solution and was slightly lower in the case of filtration of the real fermentation solution ($\alpha = 0.56$) than the value determined for filtration of the model solution ($\alpha = 0.62$).

In the final part of the study it was attempted to regenerate the membranes in the following sequence of the selected solutions: deionized water (stage I), an alkaline solution (stage II), acidic solution acid (stage III) and again alkaline solution (stage IV). The lowest efficiency within this sequence was observed in the first stage of the regeneration, this is washing the membrane with deionized water (Fig. 4). This was observed both in the case of the membrane used for filtration of the real fermentation, as well as for the membrane used for filtration of the model solution. It should be noted that in the case of the membrane used to filter the real fermentation solution it was found that filtration of deionized water resulted in approx. 12 % increase in its performance (Fig. 5). This confirms the initial assumptions regarding the occurrence of fouling, which was partially reversible. Chemical cleaning in the base-acid-base sequence, which was used afterwards, resulted in a significant increase in the performance of both tested membranes. In the case of the membrane used for filtration of the real solution regeneration was achieved in 96 %, and for the membrane for the filtration of the model solution the initial performance was restored in 100 %.

The obtained results confirm the high efficiency of chemical methods in the regeneration process of membranes fouled due to filtration of fermentation solutions. Rinsing the membrane with deionized water, in this specific case, was found to be virtually inefficient. In the case of chemical cleaning of the membranes it is crucial to use the reagents in a proper sequence, depending on the type of substances responsible for fouling (organic and/or inorganic). In this case the alkaline solution reacts with the organic substance and the acidic solution with the inorganic substance and to some extent with the organic substance [5]. The sequential use of these reagents markedly increases the efficiency of removing impurities from the surface of the membrane, which is particularly important when the retained precipitates have a multilayer structure.

Conclusion

1. The AFC-30 membrane possesses separation characteristics similar to the membranes used in reverse osmosis. The determined transport properties of the membrane allow, however, classifying it as a typical nanofiltration membrane.

2. The hydraulic efficiency of the membrane is lower in the case of filtering the real fermentation solution, than that observed for the model solution. This is due to the fact that the nature of the feed is essential for the occurrence and the mechanism of blocking the membrane pores.

3. Regeneration of the membrane surface fouled after filtration of the fermentation solutions requires the use of chemical methods, in the sequence of base-acid-base. In the studied case rinsing the membrane with deionized water only was virtually ineffective.

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NANOFILTRACJA ROZTWORÓW FERMENTACYJNYCH – ZJAWISKA NIEKORZYSTNE ORAZ CZYSZCZENIE MEMBRAN

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Abstrakt: Oceniono intensywność niekorzystnych zjawisk występujących podczas procesu nanofiltracji roztworów fermentacyjnych oraz zbadano możliwość czyszczenia membran po filtracji membranowej. Prace prowadzono z wykorzystaniem modułu rurowego wyposażonego w membranę AFC-30. Filtrację przeprowadzono pod ciśnieniem transmembranowym 2,0 MPa, przyjmując prędkość liniową nadawcy 3,4 m/s oraz temperaturę filtrowanego roztworu równą 20 °C. Wydajność hydrauliczną membrany badano zarówno podczas filtracji roztworów modelowych, jak i rzeczywistych. Określono warunki prowadzenia efektywnego czyszczenia zanieczyszczonej powierzchni membran metodą chemiczną z użyciem różnych reagentów. Membranę próbowano również płukać czystą wodą. W zakresie badań wstępnych wyznaczona została charakterystyka transportowa i separacyjna membrany AFC-30 dla wody zdejonizowanej oraz roztworów soli NaCl i $MgSO_4$ reprezentujących odpowiednio jony jedno- i dwuwartościowe. W tym przypadku właściwości membrany badano w zmiennych warunkach ciśnienia transmembranowego od 1,0 do 2,0 MPa.

Słowa kluczowe: nanofiltracja, roztwory fermentacyjne, obniżenie wydajności hydraulicznej membrany, czyszczenie powierzchni membran

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CHANGEABILITY OF HEAVY METALS CONTENT IN THE SEDIMENT OF THE WATER RESERVOIR IN THE 1996–2005 YEARS

ZMIENNOŚĆ ZAWARTOŚCI METALI CIĘŻKICH W OSADACH DENNYCH ZBIORNIKA WODNEGO W LATACH 1996–2005

Abstract: The presented study was aimed to analyze the variability of the selected heavy metal content in bottom sediments from a dam reservoir in Krempna, located in the upper part of the river Wisloka, in the Subcarpathian Voivodeship. The concentrations of the analyzed heavy metals in the examined sediments were variable. The copper content ranged from 8.4–49.16 mg · kg^{-1}, zinc 28–98 mg · kg^{-1}, chromium 8.7–70 mg · kg^{-1}, nickel 20.53–74.5 mg · kg^{-1}, lead 7.7–64.3 mg · kg^{-1} and cadmium 0.1–0.6 mg · kg^{-1}. The heavy metal concentrations in the bottom sediments of the Krempna reservoir were referred to the limit values that inform whether the material is contaminated. The contents of heavy metals did not exceed the limit content. The analyzed material was characterized by elevated concentrations of copper, chromium, nickel and lead, far beyond the geochemical background of the Polish sediments given by the Polish Geological Institute. Particularly high concentrations of nickel qualify the sediment as the class III, ie as contaminated. In the analyzed study period of 1996–2005 the bottom sediments showed no clear tendency to excessive accumulation of the examined elements. Heavy metal concentrations fluctuated in different years of the sediment collection, however there was no clear decreasing or increasing trend.

Keywords: bottom sediments, heavy metals, dam reservoir

Heavy metals, due to their specific characteristics, are a potential threat to all living organisms. They can occur in different forms in aquatic environment: as water-soluble compounds or associated with the particles of the solid phase (mineral suspension of bottom sediments) [1]. Soluble forms of metals are precipitated as a result of oxidation processes, creation of different chemical compounds and sorption by organic and

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mineral fraction of sediments. At present, the chemical composition of sediments is significantly affected by the intensity of agricultural use of catchments, by elution of residues of fertilizers and plant protection products from fields and meadows, transportation, dust emissions and sewage discharge, which leads to the increase in the heavy metal concentration in sediments [2–5]. Despite the temporary immobilization of metals in sediments, they are a potential threat to the aquatic environment.

Geochemical composition of sediments accumulated on the bottom of rivers and reservoirs is a good indicator of surface water purity [6, 7]. Observation of changes in sediments allows to determine the changes occurring in watercourses.

Properties of sediments from running waters are different than those from stagnant water sediments. Sediments from artificial reservoirs, which are intermediate between rivers and lakes, are characterized by yet other qualities. Dam reservoirs are strongly influenced by the catchment's morphology, hydrological conditions, chemical composition of water, as well as by flora and fauna of the supplying streams [8]. Hydrological conditions, especially changes in water flow velocity in the dammed river section affect the diversity of heavy metal content in the reservoir's sediments [9]. High water levels in rivers and streams flowing directly into reservoirs cause significant leaching of chemicals, removing of soil material from catchments and introducing of nutrients. The deposition of heavy metal-contaminated slurry onto floodplain soils during floods or due to excavation of sediments during dredging of reservoirs constitutes a threat to the terrestrial environment [10].

Silting of reservoirs is one of the main limiting factors for their proper operation. Small objects are particularly exposed to rapid loss of capacity in favor of the fine-grained mineral material accumulated in the reservoir bowl [11, 12]. The analysis of the heavy metal concentration accumulated in bottom sediments allows to identify the source, speed and the route of distribution of elements in the reservoir and is the basis for determining the secondary water pollution . This is particularly important in the case of small reservoirs, due to the rapid rate of silting and the necessity of periodic dredging of these reservoirs [13].

This study was aimed to investigate the variability of the selected heavy metal concentration in bottom sediments from the dam reservoir in Krempna, located in the upper part of the river Wisloka.

Material and methods

Bottom sediments were collected 4 times in the period of 1996–2005 from the dam reservoir located in Krempna. Bottom sediment samples were collected within three zones of the reservoir: at the inlet, in the middle and at the outlet (near-dam zone). The sampling sites were located outside the flow riverbed and three samples from each zone were collected (Fig. 1). The material was sampled from under the water table using the Ekman's bottom sediment probe. In order to average the sampled material, 6 subsamples were collected, which then were mixed to form the final sample. The sediments were collected from the 0–15 cm layer.

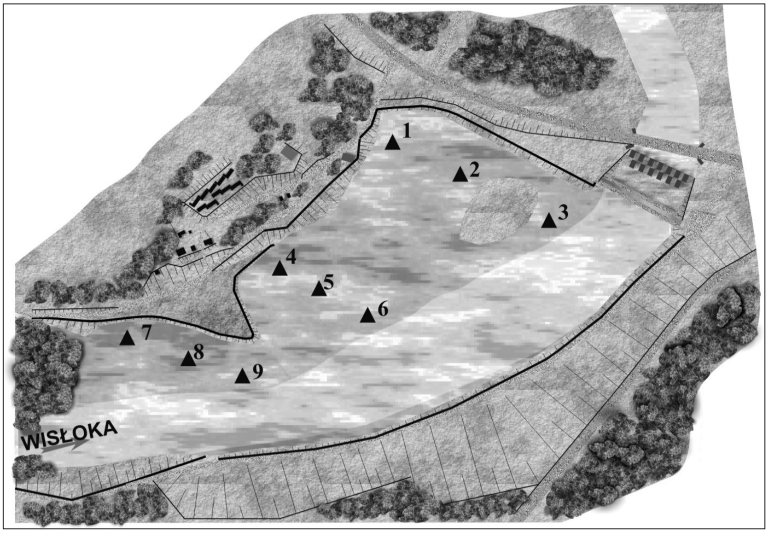

Fig. 1. The plan of the Krempna reservoir on the Wisloka river with marked bottom sediment sampling sites

The resulting material was dried and the concentration of chromium, nickel, copper, zinc, cadmium and lead was determined by AAS. The results were subjected to statistical analysis using a repeated measures ANOVA and HSD Tukey's test, using the R software for the calculations and drawing graphs [14].

The studied object is located in the Krempna locality, 35 km from Jaslo, on the river Wisloka, which is the second order tributary of the Vistula. The total length of the Wisloka is 163.6 km and the catchment area is 4110.2 km^2. To the Krempna locality, where the reservoir is located, the river is only 18.6 km long. The reservoir's dam closes the sub-catchment with an area of 165.3 km^2, located in the south-western part of the Subcarpathian Voivodeship.

The upper Wisloka catchment is located within the Magura Nappe, which is mostly composed of slate and sand flysch. The surface formations in this area are composed of residual and slope clays, formed by physical weathering of bedrock. These are medium deep soils, mostly acidic with low nutrient content. The catchment area is predominated by woodlands. The forest-occupied area accounts for about 80 % of the catchment, which is due to its mountainous nature. A significant part of forests is included in the Magura Nature Park. Meadows and pastures are often situated in gentle hills or less steep slopes (14 %). Difficult growing conditions and infertile soils limit the agriculturally used land to small areas of gentle slopes and locally wide bottoms of the river Wisloka. The total area of arable land represents only 4 %, the remaining *ca* 2 % of the catchment is occupied by roads and less crowded, mostly rural, housing [11].

The reservoir in Krempna, located in the upper part of the Wisloka river in km 145 + 023 of its course, was put into operation in 1972. The reservoir, which was constructed at the request of the Krempna Municipality, plays recreational functions and enables the operation of a small hydropower plant. A 145 m long earth dam, with a four-span concrete weir, acts as the damming element. Below the existing reservoir there will be a designed large Katy-Myscowa reservoir. The reservoir in Krempna will serve as the preliminary reservoir.

In the first period of operation, the flooding area was about 3.2 ha and the volume was 119.1 thousand m^3. In 1987–1988 and in 2005 renovation works were carried out, because of the significant silting of the reservoir. Bottom material was partially deposited in the reservoir bowl, forming a left-bank beach and was disposed of on local farms.

Results and discussion

The examined sediments were characterized by varying concentration of the analyzed heavy metals (Fig. 2). The concentration of copper over the study period ranged from 8.4 to 49.16 $mg \cdot kg^{-1}$. The least variable concentrations of copper in all analyzed samples were recorded in 2002. The lowest content was recorded in 1996 in the section located at the inlet to the reservoir. Within ten years of the study, the concentration of zinc was 28–98 $mg \cdot kg^{-1}$. The concentration of this metal was the highest in 2002, particularly in the sites located near the inlet and the mainstream. These values were about 40 % higher than those obtained in 1996. The smallest amounts of zinc were found in the sediment samples collected in the first year of the study. The content of chromium ranged from 8.7 to 70 $mg \cdot kg^{-1}$. The smallest amounts of chromium, recorded in 1999, were over twice lower than the ones obtained in 2002 and 1996, and over 4-times lower than the values recorded in 2005. Accumulation of this metal increased at the outlet from the reservoir. The nickel content ranged from 20.53 to 74.5 $mg \cdot kg^{-1}$ over the whole study period. The highest concentrations were recorded in 2002 in all samples, while a significant decrease was observed in 2005. The concentrations of lead ranged from 7.7 $mg \cdot kg^{-1}$ to 64.3 $mg \cdot kg^{-1}$ over the study period. The highest value (about 60 $mg \cdot kg^{-1}$) was observed in the first year of the study at the outlet from the reservoir. The remaining results were similar to each other. The cadmium concentrations ranged from 0.1 to 0.6 $mg \cdot kg^{-1}$. The cadmium concentration was even over the 9-year period in the examined sediment samples at the outlet of the reservoir. The highest cadmium concentration was recorded in 2002 at the inlet – it was almost 2–4-times higher than in 1996.

The repeated measures ANOVA test was performed, in order to show statistically significant differences between the values detected in each year of the study for the selected heavy metals. The calculated test statistics (F) and probability values (p) (Fig. 2) indicate a rejection of the null hypothesis for all analyzed groups of elements (Cu, Zn, Ni, Cr, Pb, Cd) in favor of the alternative hypothesis and thus demonstrate the differences between the groups in different years. Moreover, a HSD Tukey's test was performed – a so-called post-hoc test, used when the analysis of variance (ANOVA) showed that the groups are significantly different. HSD is used to indicate the differing groups. The test involves the calculation of a "p" value for each pair of groups, which indicates the significantly different pairs, when it is lower than 0.05 (Table 1).

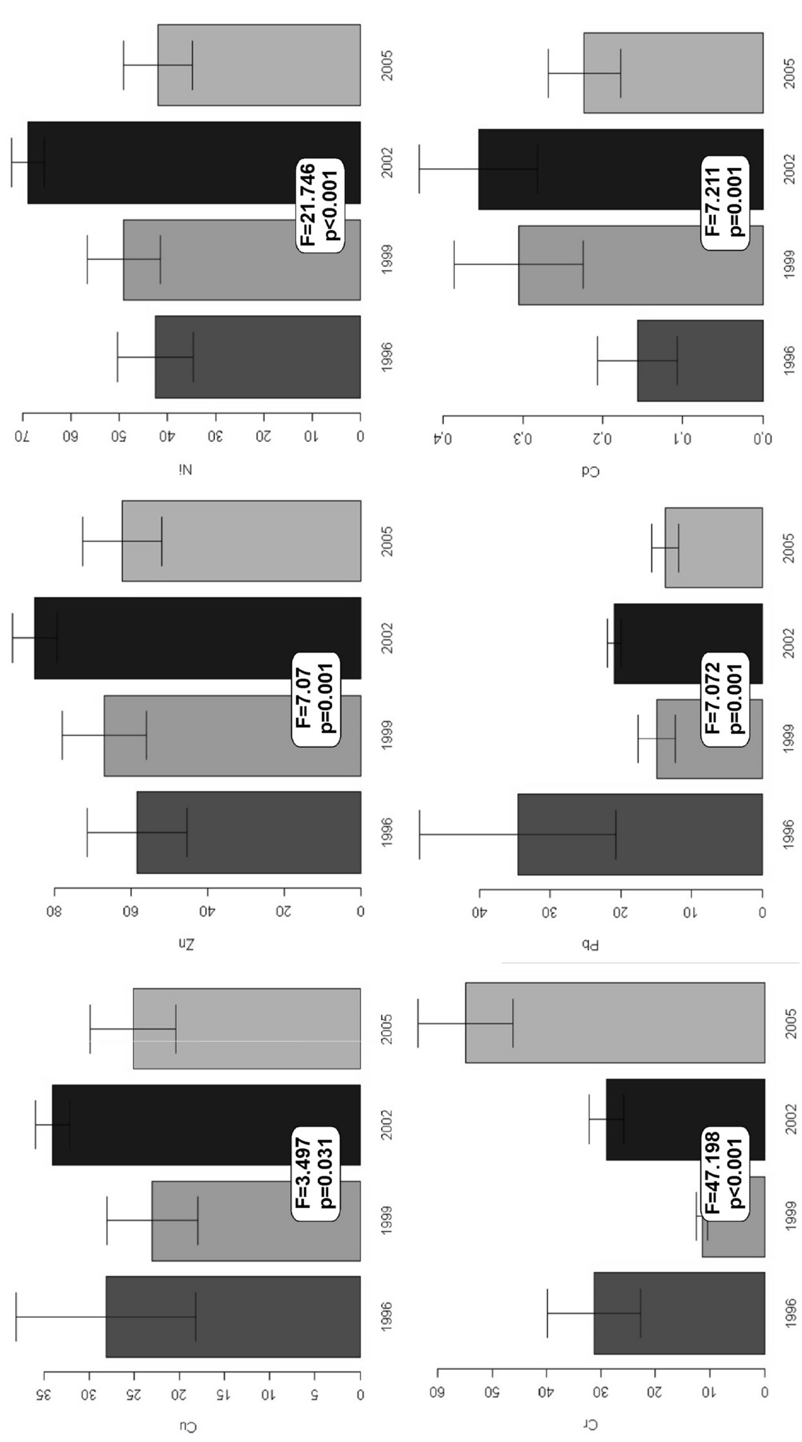

Fig. 2. Mean values and the values of the confidence interval and ANOVA statistics for the examined heavy metals in each year of the study

Table 1

Summary of "p" values calculated using the HSD test for heavy metals analyzed in each year of the study

Year	1996	1999	2002	2005	1996	1999	2002	2005
	Cu				Zn			
1996	—	—	—	—	—	—	—	—
1999	0.487	—	—	—	0.531	—	—	—
2002	0.365	**0.013**	—	—	**< 0.001**	**0.02**	—	—
2005	0.84	0.935	0.067	—	0.928	0.882	**0.002**	—
	Cr				Ni			
1996	—	—	—	—	—	—	—	—
1999	**< 0.001**	—	—	—	0.32	—	—	—
2002	0.924	**< 0.001**	—	—	**< 0.001**	**< 0.001**	—	—
2005	**< 0.001**	**< 0.001**	**< 0.001**	—	0.999	0.257	**< 0.001**	—
	Pb				Cd			
1996	—	—	—	—	—	—	—	—
1999	**< 0.001**	—	—	—	**0.008**	—	—	—
2002	**0.037**	0.645	—	—	**< 0.001**	0.702	—	—
2005	**< 0.001**	0.995	0.489	—	0.475	0.286	**0.022**	—

The changes in heavy metal concentrations in the sediments were most significantly influenced by the pre-sampling period in 2002. In 2002, a statistically significant increase in the concentration of Cu, Zn and Ni was recorded in the sediments, as compared to other years of the study, but this increase occurred only once and the heavy metal contents decreased in subsequent years.

When analyzing the cadmium concentrations, the statistically significant differences were detected between the concentrations recorded in 1996 and 1999, and 2002, as well as the difference between 2002 and 2005. This indicates that the situation is quite dynamic. In 1999 and 2002 the concentration of cadmium in the sediment samples was significantly higher than in 1996, then it declined significantly in 2005, as compared to 2002.

There are statistically significant differences between 1996 and the other years of the study shown in the analysis of lead concentration. This indicates that in 1999 there was a statistically significant decrease in the concentration of lead in the sediment and the resulting situation was sustained, as from the beginning of that year there were no statistically significant differences recorded.

There was a high change rate concerning the variability of chromium concentration in the examined sediments of the Krempna reservoir. There is a non-significant difference only between 1996 years and 2002 years. This means that in 1999 a significant decrease in chromium concentration was recorded, but this decrease occurred only once, and in 2005 there was a significant increase in the chromium concentration in the sediments.

The variability of the analyzed content of trace elements in the bottom sediments is influenced by the nature of the reservoir and the watercourse on which it is located. The examined object is a small reservoir on a river with large and abrupt floods. The resulting marginal left-bank part of the reservoir reduces the flow velocity and causes intense sedimentation of saltations, particularly in the phase of descending high water waves.

The examined heavy metal content in the bottom sediments of the reservoir in Krempna was referred to the limit values that inform whether the material is contaminated [15]. The concentration of copper, zinc, chromium, lead and cadmium was much lower than the limit values provided by the Act, the nickel content was higher, particularly in 2002 (63.5–74.5 mg · kg^{-1} d.m.), nevertheless it still did not exceed the threshold value.

Polish Geological Institute introduced a qualitative classification of bottom sediments, determining the thresholds of accumulated pollutants that affect the life processes of aquatic organisms (class I – slightly polluted sediments, class II – moderately polluted sediments, class III – polluted sediments) [6]. Exceeding the limit given for at least one harmful compound defines the sediment's quality (Fig. 3).

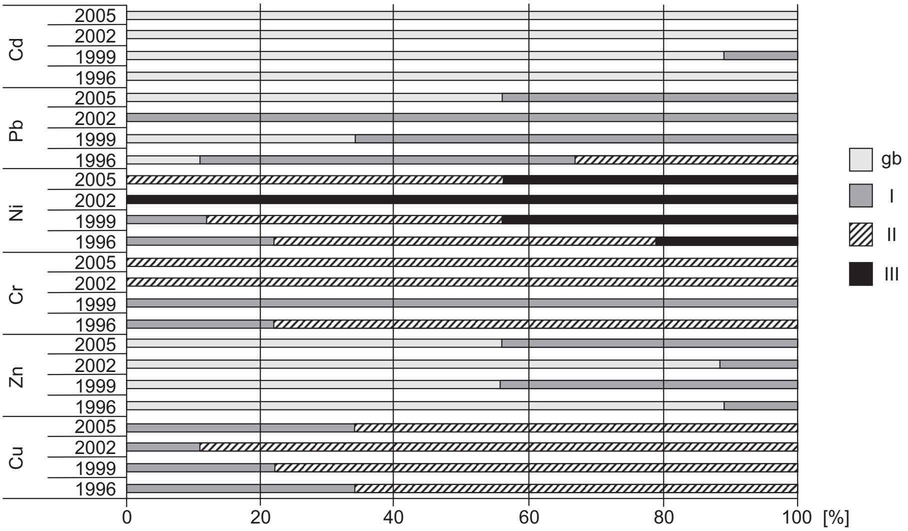

Fig. 3. Percentage contribution of the investigated sediments according to geochemical classification in particular years of the study; gb – geochemical background

The material collected in 1996 was moderately polluted in terms of copper, chromium and lead (class II), while in terms of the zinc concentration, the sediment was included into class I. In 1999 the bottom sediment contained lower concentrations of chromium and lead, therefore it was classified as moderately polluted. In 2002 the amounts of chromium increased to the level of the class II of pollution, while copper, zinc and lead remained at the same level. This trend was sustained in 2005. The concentration of nickel in the sediment collected over the period of 1996–2005 was very high, therefore it was evaluated as the class III. The cadmium content was low – of all collected samples only one was characterized by the exceeded geological background.

Conclusions

1. The examined bottom material showed no clear tendency to excessive accumulation of the analyzed elements during the period of 1996–2005. Metal concentrations fluctuated in different years, there were no clear decreasing or increasing trends, though.
2. The sediment from the examined reservoir was characterized by excessive content of copper, chromium, nickel and lead.
3. Due to the significant excess of nickel, the sediment was qualified as class III, ie as polluted.
4. Research on bottom sediments should be continued because of the potential risk to the running water, as this material is the best indicator of environmental risk. This will also allow to control the chemical composition of the material, which is disposed of by farmers on nearby agricultural lands.

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ZMIENNOŚĆ ZAWARTOŚCI METALI CIĘŻKICH W OSADACH DENNYCH WYBRANEGO ZBIORNIKA WODNEGO W LATACH 1996-2005

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Abstrakt: W pracy badano zmienność zawartości wybranych metali ciężkich w osadach dennych pochodzących ze zbiornika zaporowego w Krempnej, zlokalizowanego w górnym odcinku rzeki Wisłoki, w województwie podkarpackim. W latach 1996–2005 osad pobierano 4-krotnie. W uzyskanym materiale oznaczono zawartości chromu, niklu, miedzi, cynku, kadmu i ołowiu metodą ASA. Badane osady charakteryzowały się zmiennym stężeniem analizowanych metali ciężkich. Zawartość miedzi była w zakresie 8,4–49,16 mg $\cdot$ kg^{-1}, cynku 28–98 mg $\cdot$ kg^{-1}, chromu 8,7–70 mg $\cdot$ kg^{-1}, niklu 20,53–74,5 mg $\cdot$ kg^{-1}, ołowiu 7,7–64,3 mg $\cdot$ kg^{-1}, kadmu 0,1–0,6 mg $\cdot$ kg^{-1}. Stężenia badanych metali ciężkich w osadzie dennym zbiornika w Krempnej odniesiono do wartości dopuszczalnych, które powodują, że urobek jest zanieczyszczony. Zawartości metali ciężkich nie przekraczały zawartości dopuszczalnych.

Analizowany materiał wykazywał podwyższone stężenia miedzi, chromu, niklu i ołowiu, znacznie przekraczające tło geochemiczne osadów Polski wg PIG. Szczególnie wysokie stężenie niklu kwalifikują osad do III klasy jako zanieczyszczony. W analizowanym okresie badawczym 1996–2005 materiał denny nie wykazywał wyraźnych skłonności do nadmiernej kumulacji oznaczonych pierwiastków. Stężenia metali ciężkich ulegały wahaniom w poszczególnych latach badań, stwierdzono brak jednoznacznych trendów malejących czy rosnących.

Słowa kluczowe: osad denny, metale ciężkie, zbiornik zaporowy

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MODELLING OF STORMWATER QUANTITY AND QUALITY ON THE EXAMPLE OF URBANISED CATCHMENT IN KIELCE

MODELOWANIE ILOŚCI I JAKOŚCI ŚCIEKÓW DESZCZOWYCH NA PRZYKŁADZIE ZLEWNI ZURBANIZOWANEJ W KIELCACH

Abstract: Due to the stochastic character of precipitation phenomena, and also the accumulation of pollutants in the catchment area and their washoff, predicting the stormwater quantity and quality is a very complex task. That can lead to massive calculation errors at selection and design stages of technological lines in stormwater treatment plants. For hydraulic sewerage systems, the guideline ATV A-118 and the PN-EN 752 standard recommend using hydrodynamic modelling for the catchment area of more than 200 ha, but also for cases when surface flooding caused by excess stormwater occurs, which happens quite often in urban areas. As a majority of computational software tools (SWMM, Mouse, Mike Urban, Civil Storm), in addition to modules for runoff simulations also have those dedicated to wastewater quality assessment, it is justifiable to conduct complex analyses. The paper aims to discuss the results of stormwater quality and quantity numerical simulations obtained with the SWMM software for Si9 sewer catchment located in the area of Kielce. For the paper, hydrogram computations were made for the catchment runoff and the suspension concentrations at the assumption of constant intensity of the rainfall of the duration of t_d = 15–180 min and the precipitation occurrence probability of p = 20 %. In addition, a mathematical model of stormwater treatment plant was developed. That allowed the determination of the pollutant load of the existing technological line, and of volume and load of suspended solids discharged by the stormwater overflow structure directly into the receiver. The computations that were conducted showed a limited impact of a specific runoff on the mass of suspended solids delivered from the catchment under consideration.

Keywords: hydrodynamic modelling, SWMM, stormwater, suspended solids

Evaluating the amount of pollutant load in the stormwater discharged to the receiver is of key importance for sizing the stormwater treatment plant (STP). Both the quality

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and quantity of stormwater from the catchment determine the type and capacity of the devices used. In a majority of cases, the systems comprise a sedimentation tank or a grit chamber and a separator. At the design stage, it is necessary to account for the maximum rate of stormwater flow. When sizing the separator, the permissible concentration of suspensions at the device inlet also needs to be taken into account [1].

The basic criterion for an adequate selection of technological tools is the correct determination of the amount of stormwater delivered to the treatment facility. Although the Regulation of the Minister of Environment of 24 July 2006 [2] specifies the minimum value of runoff that must be treated ($q = 15\ \mathrm{dm}^3 \cdot (\mathrm{s} \cdot \mathrm{ha})^{-1}$), the document does not state whether constant or varied rainfall intensity should be assumed. The issue is relevant because when the quantity of runoff from the catchment is larger than the value of specific runoff stipulated in the Regulation [2], the stormwater can be directly discharged into the receiver, which can be done no more than five times a year. The Regulation [2] also gives the maximum permissible pollutant concentration in the discharge from the treatment plant. For suspensions, pollutant concentration cannot exceed $100\ \mathrm{mg} \cdot \mathrm{dm}^{-3}$, and for oil-derived substances – $15\ \mathrm{mg} \cdot \mathrm{dm}^{-3}$.

The methods commonly used in Poland for calculating the runoff hydrograms (limit rain intensity, time delay factor) involve very simplified models, and they do not account for many contributing factors. Those include, among others, variation in the catchment soil moisture during the rain event, the length of the rainless period, uneven distribution of rainfall intensity, direction of the precipitation front movement [3]. Disregarding those factors may lead to substantial computational errors [3–5], and thus to inadequate sizing of the technological devices.

In view of the foregoing, it is advisable to determine the quantity and quality of stormwater through mathematical modelling [6–9]. The existing stochastic models [10–12], however, are usually local in nature, and the parameters defined in those will be significantly changed for each catchment, which leads to erroneous predictions. Deterministic models [7, 13], which provide the opportunity to examine the effect of various parameters on the results obtained, constitute another group. In those models, however, it is necessary to know many input data describing the accumulation of pollutants on the catchment surface and the washoff of pollutants in precipitation events. The Storm Water Management Model (SWMM) is a widely used deterministic tool. It offers the possibility of determining the surface runoff and the pattern of pollutant (*eg*, suspensions, heavy metals and biogenic compounds) variation during the rain event [14].

Expotential and exponential models are often used to calculate pollutant depositions and washoff. The models are described by the respective equations:

$$B = C_1 \cdot (1 - e^{-C_2 \cdot t}) \tag{1}$$

$$W = C_3 \cdot q^{C_4} \cdot B \tag{2}$$

Literature data [6, 12, 15, 16] indicate that the values of parameters C_i employed in the equations above range as follows: $C_1 = 12.4–225.0\ \mathrm{kg} \cdot \mathrm{ha}^{-1}$, $C_2 = 0.01–5.50$, $C_3 = 0.025–0.130$, $C_4 = 1.0–2.2$. Those data confirm enormous variation, with respect to suspended solids, in quality and quantity of stormwater flowing from the catchment. In order to describe the random character of phenomena that affect the prediction of stormwater quality, the authors [17–21] developed probabilistic models, in which the stochastic character of the analysed phenomena is often accounted for by means of the Monte Carlo method.

The aim of the paper is to analyse, on the example of urbanised catchment in Kielce, the possibility of applying the SWMM software to the modelling of the quantity and quality of stormwater. The degree to which the existing STP is loaded with pollutants was evaluated. Also, the volumes of stormwater flowing from the catchment and transported to the STP, and discharged, via the stormwater overflow structure, directly to the receiver were determined. Additionally, the content of suspended solids load delivered to the STP relative to the total content of pollutants washed off the catchment surface was determined in the study.

Materials and methods

Facility description

The object of analysis is the sewer Si9 catchment, located in the central – eastern part of the city of Kielce with a total area of F = 62 ha. The sewer of concern receives stormwater and snowmelt from the part of the city lying in the left-hand side basin of the river Silnica. The total length of the sewer network is 5583 m, including the main collector (ϕ600–1250 mm) 1569 m, and lateral sewers (ϕ300–1000 mm) 4014 m in length. The slope of the collector ranges from 0.04 to 3.90 %, and that of lateral sewers is up to 2.61 %. In this area, housing estates, public buildings, main and side streets are predominant. A detailed description of the catchment can be found in studies by Dabkowski et al [22], Gorska and Sikorski [23], and Bak et al [24].

Stormwater delivered by the sewer Si9 is directed to the stormwater treatment plant, which consists of a separation chamber (SC), two-chamber settling tank (ST) and coalescence separator (SEP), which remove suspended solids and oil derivatives. When the *SC* is filled below 0.42 m (overflow height) the stormwater is transported via four sewers ϕ400 mm exclusively to the longitudinal settling tank, which has a length of 30 m. The stormwater from the treatment facility flows simultaneously through the sewer ϕ200 mm to the SEP, and through two sewers ϕ500 mm to the connection chamber (CC), to which stormwater is also delivered after it has gone through the separator (via the sewer ϕ350 mm). In the final stage, from the CC, the stormwater flows through the sewer ϕ650 mm to the receiver. However, when the filling of the separation chamber exceeds 0.42 m, a part of the stromwater is discharged through the overflow structure, via the collector ϕ1250 mm, directly into the receiver, which is river Silnica.

The ultrasonic flow meter (TELEDYNE ISCO 2150) measuring the stormwater flow rate is installed in the sewer Si9, at a distance of about 7 m above the separation chamber. The stormwater samples were collected using ISCO 6712 automatic sampler.

At approx. 2 km from the northern border of the catchment, a rainfall gauging station is located [22–24].

Methodology of investigations

To make computations of the quantity and quality of stormwater, the hydrodynamic model of the sewer Si9 catchment was constructed using the SWMM software. Detailed information on the software tool can be found in studies by Huber and Dickinson [7], Zoppou [8], Rossmann [25], Zawilski and Sakson [26]. The hydrodynamic model used in the investigations consists of 92 partial catchments, the areas of which range from 0.12 ha to 2.10 ha, 200 sewerage wells and 72 sewer segments (Fig. 1). The content of sealed area in individual partial catchments ranged from 5 to 85 %, additionally, it constituted 53 % of the total catchment area. To calibrate the model, the results of the tests on the quantity and quality of stormwater (suspended solids) from the period of three years were used.

Fig. 1. Diagram of the urbanized catchment of the sewer Si9

To assess the degree of the fitting of runoff hydrograms, those measured and obtained from numerical simulations, the following parameters were used:

– the ratio of the measured surface runoff volume to that obtained by simulations:

$$R_V = \frac{V_{c(\text{pom})}}{V_{c(\text{sym})}} \tag{3}$$

– the ratio of the peak values of flow rate:

$$R_Q = \frac{Q_{d\ \max(\text{pom})}}{Q_{d\ \max(\text{sym})}} \tag{4}$$

– Nash coefficient:

$$\mathrm{NC} = \frac{\sum_{i=1}^{n} (Q_{i(\mathrm{pom})} - Q_{i(\mathrm{sym})})^2}{\sum_{i=1}^{n} (Q_{i(\mathrm{sym})} - Q_{i(\mathrm{sr,\,pom})})^2} \tag{5}$$

To describe the process of pollutant accumulation and washoff from the surface of the catchment of concern, the respective equations (1) and (2) were employed. Parameters C_1, C_2, C_3 and C_4 in the equations were determined by the model calibration. The model of stormwater treatment plant was constructed and the values of local resistances at inlets and outlets of the sewers were provided on the basis of field measurements, the planning document, and photographic images. Due to the fact that the sewers connecting different objects of the facility may be pressurised, the main force model was employed for analyses. The model makes it possible to determine the flow resistances in the sewers on the basis of indicated surface roughness. In the model, the settling tank and the separator are defined as detention tanks.

Pollutant loads

On the basis of computations performed with the SWMM software, the mass of suspended solids (pollutant load given in kg) delivered from the catchment was obtained from the following formula:

$$M = \frac{(l_i + l_{i+1})}{2} \cdot \Delta t \ \text{[kg]} \tag{6}$$

Additionally, the percentage content of the following quantities was calculated: the volume of stormwater flowing to the STP (V_{STP}) relative to the total volume the high water stage (V_c), mass of the suspension transported to the STP (M_{STP}) relative to the total mass of mineral pollutants delivered by the sewerage system (M_c). Those parameters were computed on the basis of the dependence:

$$\eta_V = \frac{V_{OWD}}{V_c} \tag{7}$$

$$\eta_M = \frac{M_{OWD}}{M_c} \tag{8}$$

Model calibration

The developed quantitative hydrodynamic model was calibrated on the basis of selected seven rainfall-runoff events of the period from July 2009 to July 2011. The characteristics of the events are presented in Table 1.

Table 1

Characteristics of the rainfall events and fitting parameters for measured and simulated hydrograms

Date	P [mm]	t_d [min]	V_c [m^3]	R_Q [-]	R_V [-]	NC [-]
08 July 2011	8.6	60	1733	0.95	0.92	0.84
15 Sept. 2010	9.2	286	2221	0.83	0.90	0.90
30 July 2010	12.5	107	1908	0.90	0.93	0.80
08 July 2009	16.5	270	3415	0.92	0.98	0.75
03 July 2009	4.2	26	2133	0.95	0.95	0.72
31 May 2010	5.4	56	684	0.90	0.90	0.70
26 April 2010	3.6	92	327	0.80	0.82	0.67

The qualitative model was calibrated using data on the 13 precipitation events measured in the time interval from 9 May 2009 until 4 June 2010. For 10 events, the ratio of the measured suspension mass to the one obtained from computations ranged 0.20–0.52, for three events (26 April 2010, 30 May 2010, 31 May 2010), the ratio was 0.97, 0.88 and 0.67, respectively. Parameters of the quantitative and qualitative models obtained by means of calibration are presented in Table 2.

Table 2

Summary of hydrodynamics model (quantitative and qualitative) parameters for the analyzed catchment

Model		Parameter	Unit	Value
Surface runoff		runoff width W	m	$1.35 \cdot F^{0.50}$
		retention of sealed areas d_{imp}	mm	1.50
		retention of unsealed areas d_{per}	mm	6.0
		roughness coefficient for sealed areas n_{imp}	$m^{-1/3} \cdot s$	0.015
		roughness coefficient for unsealed areas n_{per}	$m^{-1/3} \cdot s$	0.15
		roughness coefficient of the sewer n_{sewer}	$m^{-1/3} \cdot s$	0.015
		maximum infiltration rate $f_{\max}$	$mm \cdot h^{-1}$	90
		minimum infiltration rate $f_{\min}$	$mm \cdot h^{-1}$	15
		coefficient of infiltration decrease γ	h^{-1}	3.0
		the total time of drying out	d	3.0
Qualitative	deposition	maximum amount of pollutants accumulated in the catchment area C_{1imp}	$kg \cdot ha^{-1}$	100
		minimum amount of pollutants accumulated in the catchment area C_{1per}	$kg \cdot ha^{-1}$	35
		rate of pollutant loss C_2	d^{-1}	0.07
	washoff	washoff coefficient C_3	—	0.10
		power exponent C_4	—	1.73

In the model, constant rainfall intensity was assumed for hydrodynamic simulation. The maximum precipitation amount was determined using the Bogdanowicz and Stachy formula [3], for the rainfall duration t_d = 15–180 min (15 min time step) and event occurrence probability p = 20 %. On this basis, the specific surface runoff was determined, which is expressed as:

$$q = Q_{d\,\max} \cdot F^{-1} \quad [\mathrm{dm^3 \cdot (s \cdot ha)^{-1}}] \tag{9}$$

Results and discussion

The conducted simulations produced catchment runoff hydrograms, and also patterns of variation in concentrations of suspended solids during the events under consideration. Those made it possible to plot the figures that illustrate the effect of specific surface runoff (q) on the stormwater volume (V), instantaneous loads ($ł_i$) and mass of suspended solids (M_c) transported to the stormwater treatment plant, and also discharged through the stormwater overflow. The results of analyses are presented in Figs. 2–6.

Figure 2 indicates that an increase in q from 15.0 to 49.8 $\mathrm{dm^3 \cdot (s \cdot ha)^{-1}}$ is accompanied by a decrease in the volume of stormwater flowing from the catchment (curve A) from 9845 to 4598 $\mathrm{m^3}$ (a drop by 53.3 %). Additionally, an increase in q from 15.0 to 36.5 $\mathrm{dm^3 \cdot (s \cdot ha)^{-1}}$ results in a fall in the volume of stormwater delivered to the STP (curve B) from 6790 to 3368 $\mathrm{m^3}$ (a drop by 49.6 %). When the value of q increases, ranging 15.0–26.7 and 26.7–36.5 $\mathrm{dm^3 \cdot (s \cdot ha)^{-1}}$, for the stormwater overflow (curve C), that leads to a change in the volume of stormwater discharged directly to the receiver from 3054 to 3560 $\mathrm{m^3}$ and from 3560 to 3368 $\mathrm{m^3}$, respectively. An increase in q from 36.5 to 49.8 $\mathrm{dm^3 \cdot (s \cdot ha)^{-1}}$ is accompanied by a fall in V as regards stormwater delivered to the STP and discharged through the overflow from 3350 to 2237 $\mathrm{m^3}$ and 2362 $\mathrm{m^3}$, respectively (a drop by approx. 29.8 %).

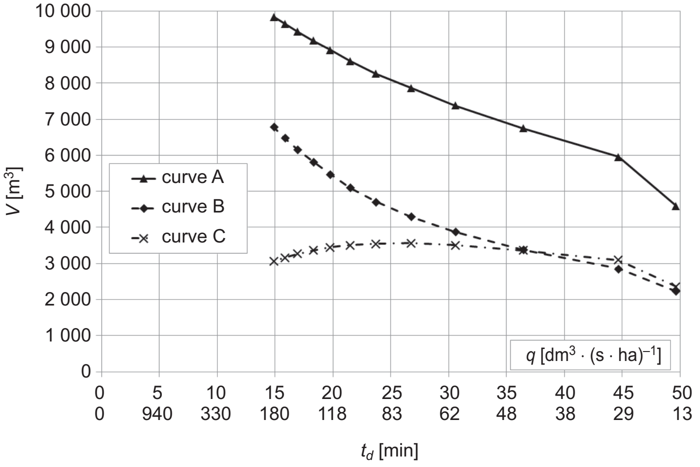

Fig. 2. Effect of specific surface runoff (q) for the rainfall duration (t_d) on the volume of storm water (V) flowing from the catchment (curve A), delivered to the STP (curve B), and discharged through the storm overflow (curve C)

The concentration of suspended solids (Fig. 3) in the range q = 15.0–36.5 $dm^3 \cdot (s \cdot ha)^{-1}$ (the same as in Fig. 2) grows from 204 to 378 $mg \cdot dm^{-3}$. For q values above 36.5 $dm^3 \cdot (s \cdot ha)^{-1}$, however, an increase in $c_{suspended}$ from 378 to 400 $mg \cdot dm^{-3}$ is observed.

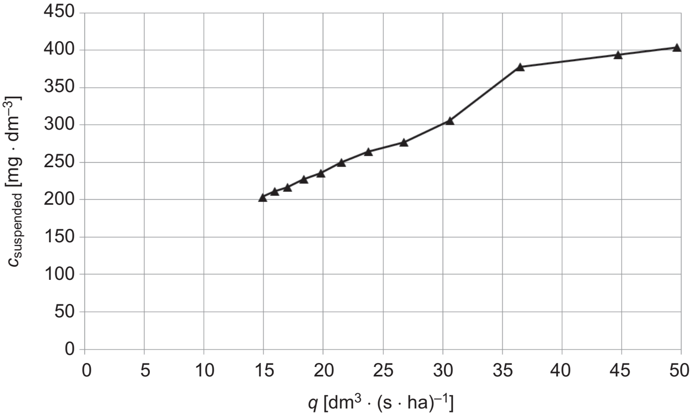

Fig. 3. Effect of specific surface runoff (q) on the maximum concentration of the suspended solids delivered form the catchment ($c_{suspended}$)

For q range under consideration, the load of suspended solids (Fig. 4) transported by sewer Si9 to the section closing the catchment (curve 1) varies in a narrow range $Ł_{max}$ = 527–589 kg. A substantial drop in the load delivered to the STP (curve 2) from 388 to 207 kg is observed when q grows. At the same time, an increase from 201 to 330 kg (curve 3) is noted in the suspension load discharged directly into the receiver.

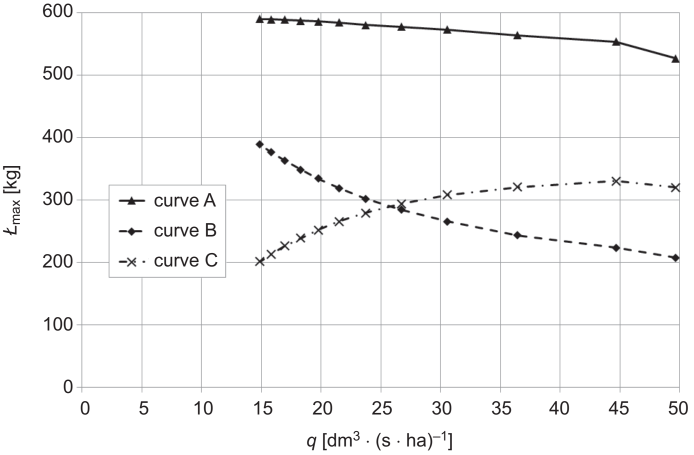

Fig. 4. Effect of specific surface runoff (q) on the load of suspended solids ($Ł_{max}$)

An increase in q value is accompanied by a drop in stormwater volume and in mass of suspended solids delivered to the STP (Fig. 5). For the maximum surface runoff that equals $q = 49.8$ dm$^3 \cdot$ (s $\cdot$ ha)$^{-1}$, treatment is applied to only 48 % of the total volume of the highwater wave, which carries merely 39 % of the total mass of pollutants.

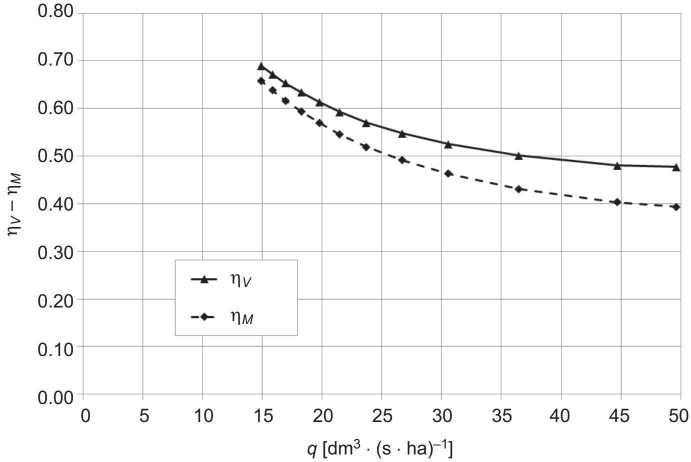

Fig. 5. Distribution, depending on q, of the volume (η_V) and mass of suspended solids (η_M) in the stormwater flowing into the STP

Figure 6 illustrates the impact of the magnitude of specific surface runoff (q) on the maximum instantaneous loads (l_{max}) of pollutants given in kg $\cdot$ s^{-1}. For instance, for $q =$ 15.0 dm$^3 \cdot$ (s $\cdot$ ha)$^{-1}$ (t_d = 180 min) and q = 36.0 dm$^3 \cdot$ (s $\cdot$ ha)$^{-1}$ (t_d = 45 min), loads of suspended solids delivered to the STP (curve A) and discharged directly to the receiver

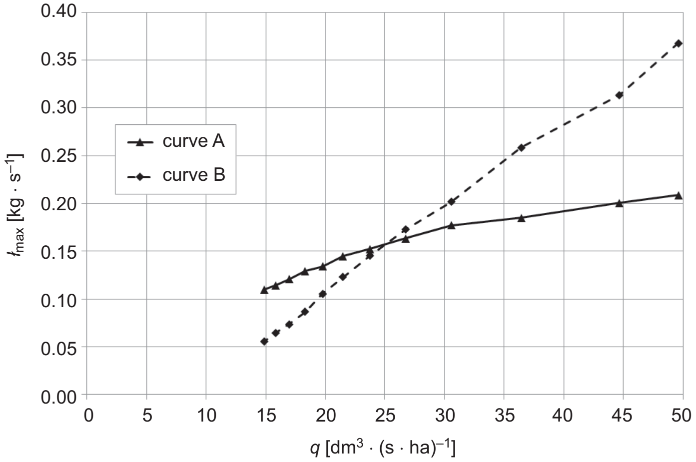

Fig. 6. Effect of specific surface runoff (q) on the maximum instantaneous loads (l_{max}) of suspended solids transported to the STP and discharged through the stormwater overflow

(curve B) amount to 0.1 and 0.06 kg · s^{-1}, and also 0.26 and 0.18 kg · s^{-1}, respectively. Additionally, it can be observed that an increase in q from 15.0 to 49.8 $dm^3 \cdot (s \cdot ha)^{-1}$ leads to an increase in $ł_{\mathrm{max}}$ transported to the STP by 90 % (from 0.11 to 0.21 kg · s^{-1}), and also more than six times increase in $ł_{\mathrm{max}}$ passing through the stormwater overflow. It should be noted that when $q = 26$ $dm^3 \cdot (s \cdot ha)^{-1}$, the maximum instantaneous loads of suspended solids are identical for both curves and are equal to 0.16 kg · s^{-1}.

Conclusions

The investigations performed for the study confirmed that the SWMM software is a suitable tool for modelling the quantity and quality of stormwater in the urbanized catchment in Kielce. On the basis of numerical simulations, the runoff and concentration ($c_{\mathrm{suspended}}$) hydrograms, and also loads of suspended solids ($Ł_{\mathrm{max}}$) washed off the catchment area were determined. The constructed mathematical model of the stormwater treatment plant made it possible to determine the amounts of stormwater flowing into individual components of the technology line, and also to compute the volume of untreated stormwater discharged directly into the receiver via the storm overflow. On the basis of the analyses, it can be stated that:

– specific surface runoff significantly affects the concentration of suspended solids contained in the stormwater washed off the catchment area; the higher is the value of q, the greater is the amount of suspended solids in 1 m^3 of precipitation water,

– the rainfall duration, at the assumption that rainfall intensity is constant, produces a low impact on the magnitude of the load of suspended solids washed off the catchment area,

– at heavy rainfalls ($q = 49.8$ $dm^3 \cdot (s \cdot ha)^{-1}$), 48 % of the total stormwater volume and 39 % of the mass of suspended solids flow into the STP,

– at moderate intensity precipitation ($q = 15$ $dm^3 \cdot (s \cdot ha)^{-1}$), approx. 69 % of the total load of suspended solids and 66 % of the stormwater volume are transferred to the STP,

– in the range $q = 15$–25 $dm^3 \cdot (s \cdot ha)^{-1}$, for the rainfall duration $t_d = 82$–180 min, instantaneous loads of suspended solids flowing into the treatment facility are higher than the values of $ł_{\mathrm{max}}$ transferred through the stormwater overflow,

– in order to reduce the amount of pollutants discharged through the stormwater overflow, it is necessary to raise the edges of the overflow structure, or to increase the throughput of the stormwater treatment plant (*ie* expand the diameters of sewers that deliver stormwater to the STP, or extend their number).

Nomenclature

B	present accumulation of pollutants [kg · ha^{-1}]
W	intensity of pollutant washoff [kg · $(ha \cdot s)^{-1}$]
C_1	maximum amount of pollutants accumulated on the catchment area [kg · ha^{-1}]
C_2	pollutant deposition velocity [$days^{-1}$]
C_3	coefficient of washoff rate [-]
C_4	power factor [-]

t	time step [s]
q	specific surface runoff [mm · h^{-1}]
R_v	ratio of the measured surface runoff volume to that obtained by simulations [-]
R_Q	ratio of the peak values of flow rate [-]
$V_{c(\mathrm{pom})}$	measured volume of runoff hydrogram [m^3]
$V_{c(\mathrm{sym})}$	volume of the runoff hydrogram obtained from simulations [m^3]
$Q_{d\mathrm{max(pom)}}$	measured peak flow [m^3 · s^{-1}]
$Q_{d\mathrm{max(sym)}}$	peak flow received from computations using the SWMM software [m^3 · s^{-1}]
NC	Nash coefficient [-]
$Q_{i(\mathrm{pom})}$	measured flow rate [m^3 · s^{-1}]
$Q_{i(\mathrm{sym})}$	flow rate obtained from simulations [m^3 · s^{-1}]
$Q_{i(\mathrm{sr,pom})}$	mean value of measured flow rate [m^3 · s^{-1}]
$l_{i,\ i+1}$	instantaneous load of pollutants [kg · s^{-1}]
V_c	total volume of stormwater determined from catchment runoff hydrogram [m^3]
V_{STP}	volume of stormwater delivered to the STP determined on the basis of simulations with the SWMM software [m^3]
M, M_c	mass of suspended solids delivered from the catchment [kg]
M_{STP}	mass of suspended solids transported to the STP [kg]
η_V	content of the volume of stormwater flowing to the STP relative to V_c [-]
η_M	content of the mass of transported suspended solids relative to M_c [-]
$Q_{d\mathrm{max}}$	maximum stormwater runoff rate [dm^3 · s^{-1}]
F	runoff area [ha]
P	total amount of precipitation [mm]
t_d	rainfall duration [min]

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MODELOWANIE ILOŚCI I JAKOŚCI ŚCIEKÓW DESZCZOWYCH NA PRZYKŁADZIE ZLEWNI ZURBANIZOWANEJ W KIELCACH

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Abstrakt: Ze względu na stochastyczny charakter zjawisk opadowych, a także akumulacji oraz zmywania zanieczyszczeń zgromadzonych na powierzchni zlewni, prognoza jakości i ilości ścieków deszczowych jest bardzo złożona, co może prowadzić do znacznych błędów obliczeniowych na etapie doboru i projektowania ciągów technologicznych oczyszczalni wód deszczowych. Wytyczna ATV A-118 oraz norma PN-EN 752 zalecają do obliczeń hydraulicznych systemów kanalizacyjnych, zastosowanie modelowania hydrodynamicznego dla zlewni o powierzchni przekraczającej 200 ha, ale również w przypadku występowania w sieci zjawiska wylania ścieków na powierzchnię terenu, co zdarza się na terenach miejskich stosunkowo często. Ponadto, ze względu na to, że w większości opracowane programy obliczeniowe (SWMM, Mouse, Mike Urban, Civil Storm) mają oprócz zaimplementowanych modułów do symulacji spływu, także moduły określania jakości ścieków, wydaje się wskazane przeprowadzenie kompleksowych analiz w tym kierunku. Celem artykułu jest omówienie wyników symulacji numerycznych jakości i ilości ścieków uzyskanych przy pomocy programu SWMM dla zlewni kanału Si9 zlokalizowanej na terenie Kielc. W artykule wykonano obliczenia hydrogramów odpływu ze zlewni i stężeń zawiesiny przy założeniu stałego natężenia deszczu dla czasu trwania t_d = 15–180 min i prawdopodobieństwa wystąpienia opadu p = 20 %. Ponadto opracowano model matematyczny oczyszczalni ścieków deszczowych, który pozwolił określić obciążenia ładunkiem zanieczyszczeń istniejącego ciągu technologicznego oraz ustalić objętość i ładunek zawiesiny ogólnej zrzucanej przelewem burzowym bezpośrednio do odbiornika. Przeprowadzone obliczenia wykazały nieznaczny wpływ jednostkowego spływu na masę zawiesiny ogólnej odpływającej z przedmiotowej zlewni zurbanizowanej.

Słowa kluczowe: modelowanie hydrodynamiczne, SWMM, ścieki deszczowe, zawiesina ogólna

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STUDY OF THE EXCESSIVE Pb-210 CONTENT IN SOIL

BADANIE ZAWARTOŚCI NADMIAROWEGO Pb-210 W GLEBIE

Abstract: The aim of the study was the analysis of soil contamination in the area in vicinity of metalworking plants located in the district Opole-Metalchem (PL). Pb-210 was used as pollution indicator because its increased concentration of activity may indicate the presence of other contaminants in the studied area. On the base of the obtained results, the activity concentration of the excessive lead was calculated. Its biggest value was observed in soil in a forest area. In areas with increased excessive lead content also elevated values of Cs-137 activity concentrations were recorded. Atmospheric source of Pb_{ex} and Cs-137 deposition was supposed.

Keywords: pollution indicator, Pb-210, soil contamination

Introduction

Industrial metalwork is one of the major sources of environmental pollution. It deals with the treatment of ores, obtaining pure metals, creating specific shapes of metal pieces and production of alloys [1]. The result of these processes is emission of a number of substances harmful to the environment and to human health [2]. One of these processes is welding, in which dust is released which contains, for example, iron oxides, manganese oxides, magnesium oxides, zinc, lead and volatile products, including sulfur oxides and carbon monoxide [3]. These substances can be dangerous for human health causing, among others, damage in neural system or induce asthma [4].

Lead and zinc alloys are one of the most important raw materials for welding. They may pose a significant threat to the health of workers and to environment. Excess amount of lead can stop production of heme and it can change routes of important biochemical processes in living organisms [5].

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Lead release during activity of various works is followed by its accumulation in soil, and then also in plants [6]. Lead accumulates in the surface layers of soil rich in humus, because it is easily incorporated into organic matter [7]. Availability of lead for living organisms depends on its chemical form in soil. Easily leached from the surface layers of soil are chlorides, nitrates, acetates, while the lead oxides are practically insoluble in water, hence immobile [8].

Lead, in particular the isotope Pb-210, may be an indicator of pollution of industrial origin. Detection of pollution is possible because its activity concentration consists of the autogenous (of natural origin) and the allogeneic (anthropogenic) part. Significant amounts of the allogeneic lead in a sample likely indicates deposition of undesired environmental pollutants [9].

The vapors produced during metallurgical processes contain, besides lead, many other heavy metals. Among them chromium, copper, lead, manganese, nickel, zinc, iron or cadmium can be listed [4–16].

In Opole-Metalchem district in the late 80. and 90. of 20th century was located great industrial center with several welding plants. The symbol of those times was Metalurgic-Chemical Plant "Metalchem" in which armaments was produced. Several thousand people were employed there and they had a housing estate specially built for them. Up to now in this area there are many welding, galvanizing and tinning works. Due to their waste production the periodic analyses of water, soil and air, are desired.

In 2013 an analysis of heavy metals content in the Odra River was carried out [17]. The object of this study was the 8.5 km section of the river, which ran among others, by Metalchem. The biggest heavy metals concentration was found in water sample collected at the river harbor on the Metalchem estate. It could be a result of the continuous pollutant rinsing from machines moored there. These are old, rusty barges and ships used formerly in transport of steel and welded structures. But it is possible that contaminants were washed out from upper soil layers by atmospheric and ground water. Determination of actual pollution sources is critical for selection of appropriate mitigation strategies which would limit impact of contaminants on environment and life quality of local population.

The aim of the study was estimation of soil contamination in the area of Metalchem. In the study Pb-210 was used as an index of pollution. The isotope Pb-210 is a natural radioactive isotope and represents the disintegration series of radioactive uranium U-238. This radionuclide may also be artificially introduced into the environment by human activities. The difference between concentrations of allogenic and autogenous Pb-210 can be regarded as a measure of total contamination of the site.

Materials and methods

The soil samples were collected at 6 places located in the south east direction from the area occupied by metalworking companies (Fig. 1).

Places No.1 and 3 were located on a meadow not far from the nearby forest. Place No. 2 was located in this forest. The remaining sampling sites were located in cornfield. The soil samples were collected from the depth of 0–15, 15–30 and 0–30 cm. The

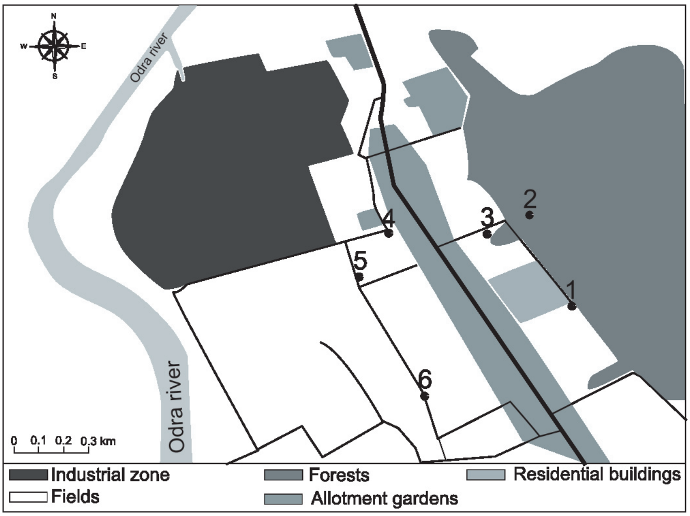

Fig. 1. Localization of sampling sites

collected samples were dried to constant mass at 105 ^{o}C, then sieved through a sieve (d = 2.0 mm) and analyzed for activity of gamma ray emitting radionuclides.

The measurements of activity concentrations was carried out by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution: 1.29 keV (FWHM) at 662 keV and 1.70 keV (FWHM) at 1332 keV. Relative efficiency: 21.7 %. Energy and efficiency calibration of the gamma spectrometer was performed with the standard solutions type MBSS 2 (Czech Metrological Institute, Prague, CZ) which covers an energy range from 59.54 keV to 1836.06 keV.

Geometry of calibration source was Marinelli (447.7 ± 4.5 cm^3) with density 0.99 ± 0.01 g/cm^3, containing Am-241, Cd-109, Ce-139, Co-57, Co-60, Cs-137, Sn-113, Sr-85, Y-88 and Hg-203. Geometry of samples container was Marinelli, 450 cm^3. Measuring process and analysis of spectra were computer controlled with use of the software GENIE 2000.

Results and discussion

In soil samples Cs-137, Pb-210, Bi-214 and Pb-214 radonuclides were determined. Table 1 contains characteristics of distribution of radionuclides specific activity concentration in the samples collected from the sites. Maximum (max), minimum (min) values, lower quartiles (Q_1), upper quartiles (Q_3), mean values ($\bar{x}$), medians (Q_2) and standard deviations (s).

The lowest difference in activity concentrations was observed for Bi-214 in upper soil layer. Similarly, the Pb-214 isotope was rather uniformly distributed in the investigated area. Concentration of this isotopes somewhat increased in deeper soil layer. Mean concentration of Bi-214 and Pb-214 in the surface layer of soil were several times lower than the average activity in the deeper layer.

Table 1

The maximum (max), minimum (min) and mean ($\overline{x}$) values of activity concentrations of the determined radionuclides. Additionally the values of standard deviation (s), median (Q_2), lower (Q_1) and upper (Q_3) quartiles are shown

Layer thickness	Radio-nuclide	Min	Max	$\overline{x}$	s	Q_1	Q_2	Q_3
		Bq/kg d.m.						
0–15	Bi-214	9.11	10.8	0.65	9.53	9.65	9.92	9.11
	Pb-214	7.43	11.7	1.77	9.48	9.82	11.7	7.43
	Cs-137	78.3	524	174	84.5	97.3	172	78.3
	Pb-210	11.1	104	33.8	21.3	30.4	45.8	11.2
15–30	Bi-214	7.54	20.2	5.83	8.48	9.98	17.9	7.54
	Pb-214	8.21	23.2	6.13	9.98	11.0	16.7	8.21
	Cs-137	18.3	102	31.2	35.4	42.1	70.2	18.3
	Pb-210	2.38	35.6	12.8	14.1	23.5	31.4	2.38
0–30	Bi-214	7.12	23.4	11.5	6.19	8.01	8.76	12.2
	Pb-214	7.47	23.3	12.2	5.76	9.19	10.1	12.6
	Cs-137	39.2	233	97.6	72.7	50.1	72.7	112
	Pb-210	14.4	41.4	25.2	9.51	19.1	25.3	27.3

The activity concentrations of Pb-210 and Cs-137 were significantly higher in the surface soil layer, reaching 104 Bq/kg d.m. and 524 Bq/kg d.m., respectively. The range of activity concentration changes was the biggest for Cs-137 (446 Bq/kg) in upper soil layer. The same difference for Pb-214 was lower (93 Bq/kg), but it was much bigger than the differences for Bi-214 and Pb-214.

Relationship between aactivity concentrations of the radionuclides determined in upper and lower soil layers is shown in the graphs (Figs. 2–5). In these figures the straight line shows equal values of the radionuclide activity concentrations in both layers. Comparison of Bi-214 and Pb-214 activity concentrations indicates rather similar amounts of these radioisotopes in upper and lower ground layers (Figs. 2–3).

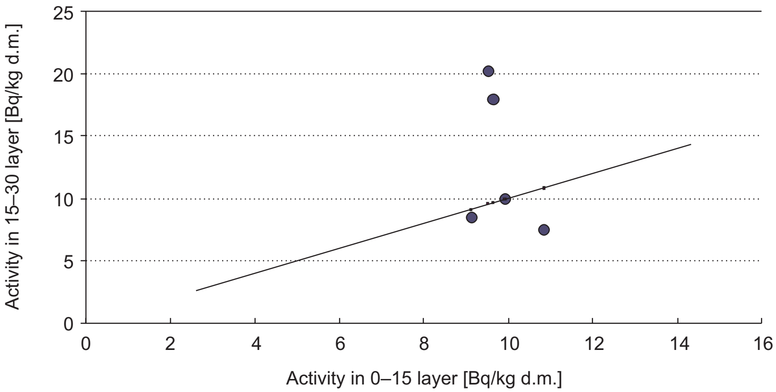

Fig. 2. Relationship between the activity concentrations of Bi-214 in upper and lower soil layer

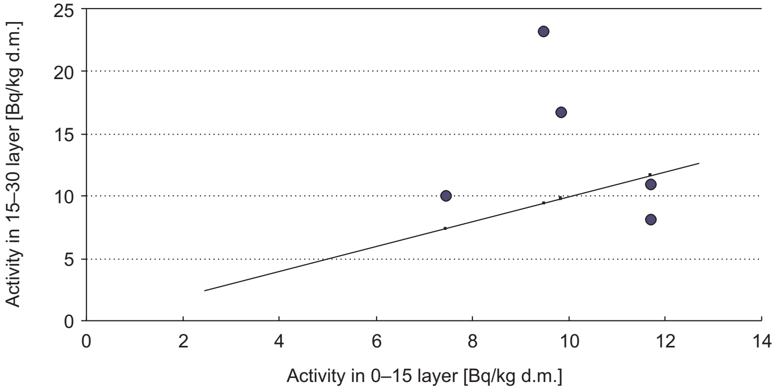

Fig. 3. Relationship between the activity concentrations of Pb-214 in upper and lower soil layer

While crops cultivation the soil layers are periodically mixed with each other as the result of ploughing. Even if mineral fertilizers supply some amounts of radionuclides, soil layer mixing in a seasonal cycles homogenizes its composition. But in opposite to Bi-214 and Pb-214, content of the Cs-137 radioisotope was considerably bigger in upper layer than in the lower. The biggest amounts of this radioisotope appeared in environment as the result of the nuclear tests carried out in 50. and 60. of 20th century [18–20]. The investigated region was additionally contaminated by Cs-137 after the explosion in Chernobyl Nuclear Power Plant in 1986 [21, 22]. Considerable amount of radiocesium was released to atmosphere as a result of the tsunami caused breakdown in Fukushima Daiichi Nuclear Power Plant in 2011 [23, 24].

In atmosphere Cs-137 was transported over long distances from contamination sources. The isotope falls down on ground surface from which it can be again blown to atmosphere. At present horizontal redistribution of Cs-137 is mainly a result of aeolian processes, though other mechanisms like forest or steppe fires should be also considered [25].

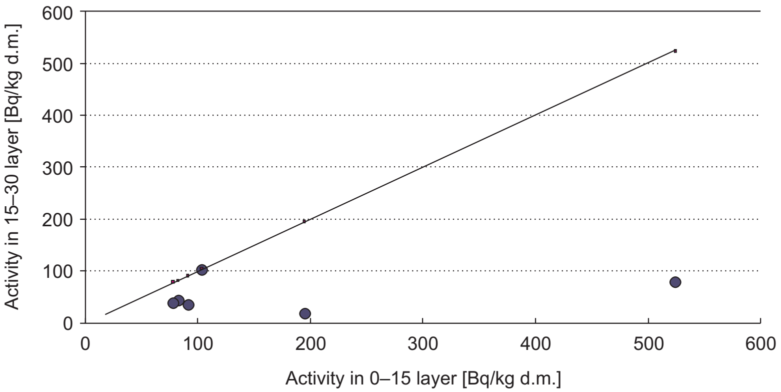

Fig. 4. Relationship between the activity concentrations of Cs-137 in upper and lower soil layer

Vertical distribution of Cs-137 in soil reflects these mechanism. The plot in Fig. 4 shows significantly bigger Cs-137 activity concentration in upper than in lower soil layer. Though cesium is transported from soil depth to surface by plants [26, 27], increased concentration of this radioisotope in the upper layer of disturbed soil justifies fallout from atmosphere as its source.

The Pb-210 radioisotope is member of the radium decay series, like Bi-214 and Pb-214. But its distribution in soil is different than that of the latter radionuclides. An increased content of this radionuclide is observed in the surface layer of the soil (Fig. 5), similarly like for Cs-137. This relationship supposes deposition of this radionuclide from atmosphere.

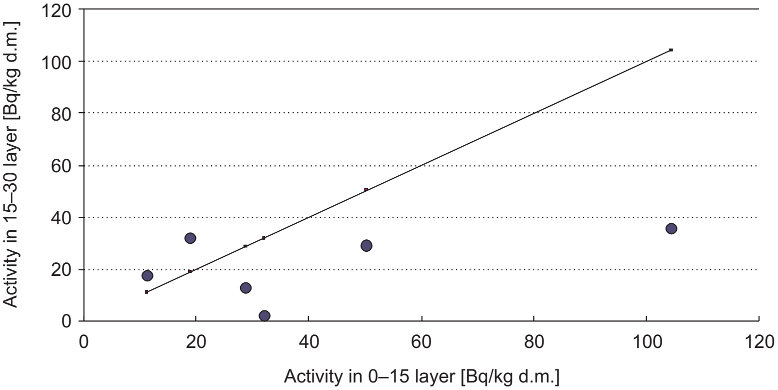

Fig. 5. Relationship between the activity concentrations of Pb-210 in upper and lower soil layer

Two different sources of Pb-210 can be distinguished – autogenous and allogeneic. Autogenous component originates from decay of Pb-210 parent radionuclides in radium series. The relatively stable ancestor of Pb-210 is Ra-226 with half-life time 1602 years. A measure of its concentration in system is activity concentration of its short living daughters, *ie* Pb-214 and Bi-214, and then the more stable Pb-210. The allogeneic component of Pb-210 appears with dust transported from distant sources, and can be regarded as the excessive lead closely associated with industrial pollutants. Presence of the two Pb-210 components enables calculation of the excessive lead content as the difference between activity concentrations of total Pb-210 and Ra-226. Further analysis was based on content of the excessive lead in soil samples. The Ra-226 activity concentration was calculated from Pb-214 and Bi-214 activity concentrations using the formula (Eq. 1):

$$a_{\text{Ra-226}} = \frac{a_{\text{Pb-214}} + a_{\text{Bi-214}}}{2} \tag{1}$$

where a is the activity concentration of radionuclide in the soil [Bq/kg d.m.].

Activity concentration of the excessive lead Pb_{ex} in the sample was calculated from Equation 2.

$$a_{\mathrm{Pb_{ex}}} = a_{\mathrm{Pb\text{-}210}} - a_{\mathrm{Ra\text{-}226}} \tag{2}$$

where: a_{Pbex} – activity concentration of the excessive lead in soil sample [Bq/kg d.m.].

The calculated lead content of the anthropogenic origin ($\mathrm{Pb_{ex}}$) in the surface soil layer was significantly higher than its content in the deeper soil layer (Fig. 6). This observation confirms atmospheric deposition of $\mathrm{Pb_{ex}}$.

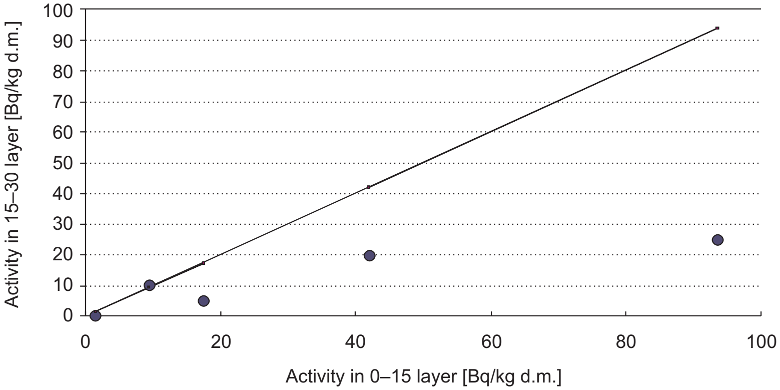

Fig. 6. Relation between the activity of $\mathrm{Pb_{ex}}$ in soil layers

The biggest activity concentration of $\mathrm{Pb_{ex}}$ was calculated in place No. 2 (32.2 Bq/kg d.m.), being the forest area. At the places No. 1 and No. 6 the activity concentrations were about half lower than at the place No. 2. In other samples $\mathrm{Pb_{ex}}$ activity concentration did not exceed 7.5 Bq/kg d.m.

In Fig. 7 relationship between activity concentrations of $\mathrm{Pb_{ex}}$ and Cs-137 in upper soil layer is shown. The straight line in the plot shows linear approximation of relationship between these parameters. Parameters of the line in the plot were calculated using the least square method.

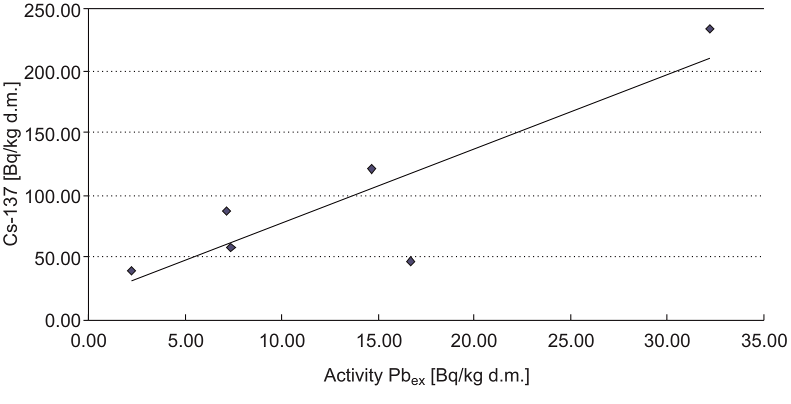

Fig. 7. Relation between the Cs-137 and the $\mathrm{Pb_{ex}}$ activity concentrations in upper soil layers

Well outlined linear relationship between Pb_{ex} content and Cs-137 activity concentration could be observed in Fig. 7. The calculated correlation coefficient was 0.87. Such a high correlation coefficient indicates a decisive influence of the local weather conditions on the accumulation of pollutants of atmospheric origin in a certain location. Though the investigated area was not big, atmospheric deposition of pollutants was highly differentiated. Inhomogeneity of soil pollution could be also a result of horizontal transport of fine matter which was floated with rain water or water from melted snow. Secondary pollutants deposition could be much more inhomogeneous than the initial pattern of atmospheric precipitation.

Conclusions

The gamma spectrometric method analysis allowed determination of two Pb-210 isotope components, the allogeneic (Pb_{ex}) and autogenous, in soil samples. Because in upper soil layer contents of Pb_{ex} and Cs-137 were well correlated, the atmospheric origin of allogeneic lead can be supposed.

The excessive lead is a good indicator of the local pollution related to dry or wet atmospheric deposition. It can be used for estimation of distribution pattern of contaminants in an area. The allogeneic lead can be used also as an indicator of pollution transport from distant sources.

Acknowledgements

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BADANIE ZAWARTOŚCI OŁOWIU NADMIAROWEGO W GLEBIE

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Uniwersytet Opolski

Abstrakt: Celem badań była analiza zanieczyszczenia gleby w rejonie zakładów metalurgicznych w dzielnicy Opole-Metalchem. Jako wskaźnika użyto Pb-210, ponieważ podwyższona jego aktywność może wskazywać na obecność innych zanieczyszczeń na badanym terenie. Na podstawie uzyskanych wyników obliczono aktywność ołowiu nadmiarowego. Największe jego aktywności zaobserwowano w glebie na terenie leśnym. W miejscach z podwyższoną aktywnością ołowiu nadmiarowego odnotowano także wyższe wartości aktywności Cs-137.

Słowa kluczowe: wskaźnik, Pb-210, zanieczyszczenie gleby

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SULPHUR IN THE FOREST SOILS OF THE OJCOW NATIONAL PARK

SIARKA W GLEBACH LEŚNYCH OJCOWSKIEGO PARKU NARODOWEGO

Abstract: The aim of this study was to determine the effect of the pedogenesis on the sulfur content in the forest soils of the Ojcow National Park (OPN). The study was carried out on soils representing the main units of OPN soil cover: brown rendzinas and soils lessives. Studied soils were characterized by a high variability of sulphate sulfur content within the profiles. The surface Ol horizons contained the highest amount of SO_4-S (in rendzinas 104.2–248.0 mg · kg^{-1}, in soils lessives 101.0–232.0 mg · kg^{-1}) and a significantly higher than deeper horizons. The concentration of sulfur in the humus A horizons was lower (in rendzinas 14.1–91.4 mg · kg^{-1}, in soils lessives 16.5–35.5 mg · kg^{-1}) and similar to the values in the horizons of parent rock (in rendzinas 12.5–26.9 mg · kg^{-1}, in soils lessives 9.1–67.5 mg · kg^{-1}). Content of SO_4-S was not varied between the Et eluvial horizons (15.9–47.3 mg kg^{-1}) and illuvial Bt horizons (12.3–49.8 mg · kg^{-1}). The direction of pedogenesis had no effect on the vertical distribution of sulfur. This set was caused probably by a high variability of relief and profiles diversity within a type unit. Moreover, the content of the analyzed component was determined by a geographical location of soils and specific microclimatic conditions of the Ojcow National Park.

Keywords: sulphur, soils, the Ojcow National Park

Introduction

The Ojcow National Park (OPN) is considered as one of the most polluted national parks in Poland for more than last three decades [1–5]. The location in the neighborhood of Silesian and Cracow agglomeration and specific climate conditions, associated with the local terrain relief, is the main reason of the high concentration of pollutants in the OPN [4, 6].

Atmospheric sulfur infiltrates into the soil with precipitation and occurs in soil in the form of sulphides and sulphates or is bound with soil organic matter. Sulphate ions may be leached from the soil or adsorbed by humic and fulvic acids, sesquioxides, clay

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minerals, as well as occluded by calcite. Transformation of sulfur is highly dependent on soil-forming processes, as well as on climatic and habitat conditions [7–11].

The study was aimed to determine the effect of the pedogenesis on the sulfur content in soils of the Ojcow National Park.

Material and methods

The soil material was taken from horizons of 23 profiles located in the Ojcow National Park. Studied soils represented the main units of soil cover of the Ojcow National Park: brown rendzinas (15 profiles) and soils lessives (8 profiles) (Fig. 1) [12, 13].

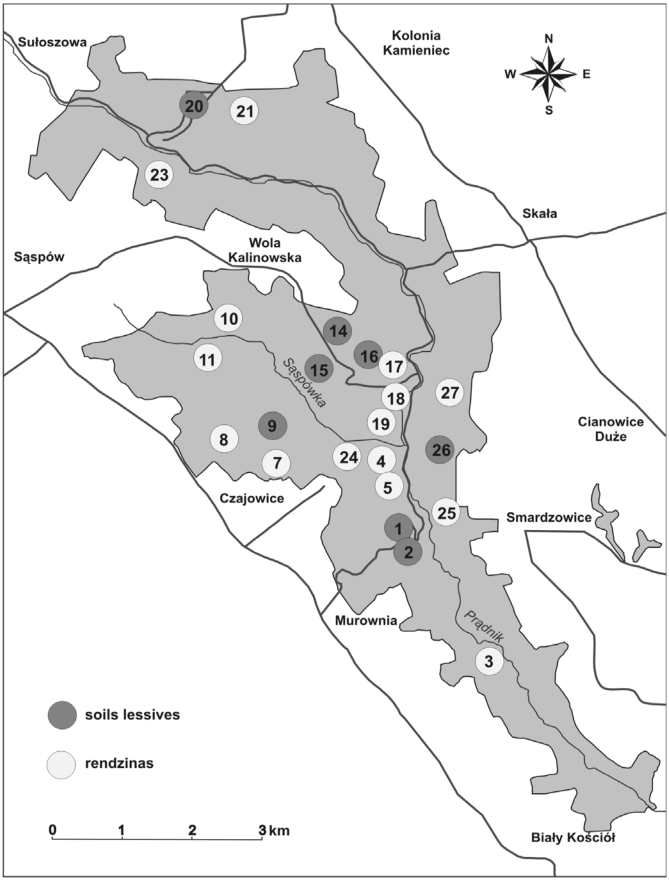

Fig. 1. Location of studied soils profiles in the Ojcow National Park

Rendzinas have been derived from Jurassic limestones and soils lessives were developed on loess sediments, underlayed by limestones. Soil profiles were located only in forests.

Soil material was dried at room temperature and sieved through a sieve with a mesh of 2 mm. The sulphate sulfur in soil was determined using the ICP-AES method after earlier extraction with a 0.3 mol · dm^{-3} HCl solution with the addition of activated carbon [9].

Spearman rank correlation coefficients were calculated between main soil parameters and sulphur content using Statistica 10.1 software [14]. The statistical differences in the sulfur content of corresponding horizons of soils lessives and rendzinas were determined using the Kruskal-Wallis test. Profile distribution of sulfur in studied soils was evaluated as well.

The sulfur accumulation index (AI) was also calculated as the ratio of its content in surface horizon (Ol or A) and in horizon of the parent rock. The maps of sulfur spatial distribution in Ol and A horizons were performed using kriging method in Surfer 8.0 software.

Results and discussion

Studied soils were characterized by a high variability of sulphate sulfur content within the profiles, what was confirmed statistically (Table 1).

Table 1

Sulphur content in studied soils (minimum, maximum, mean). Means followed by the same letters do not differ significantly ($p = 0.05$) in Kruskal-Wallis test

Horizon	Rendzinas [mg · kg^{-1}]	Horizon	Soils lessives [mg · kg^{-1}]
Ol	104.2–248.0 160.6 (a)	Ol	101.0–232.0 157.1 (a)
A	14.1–91.4 27.8 (b)	A	16.5–35.1 26.2 (b)
Cca	12.5–26.9 19.5 (b)	Et	15.9–47.3 27.8 (b)
		Bt	12.3–49.8 25.6 (b)
		C	9.1–67.5 31.5 (b)

The highest amounts of SO_4-S contained the organic surface Ol horizons. The content of sulfur in the organic horizons of rendzinas ranged from 104.2 to 248.0 mg · kg^{-1}, and in the organic horizons of soils lessives from 101.0 to 232.0 mg · kg^{-1}. In the organic horizons of soils of the Tatra National Park were determined similar values of SO_4-S content – 55.4–280 mg · kg^{-1} [15].

Sulphur content in the humus horizons was significantly lower than in the organic horizons and ranged in rendzinas from 14.1 to 91.4 mg · kg^{-1} and in soils lessives from 16.5 to 35.5 mg · kg^{-1}. In the parent rock horizons were determined similar amounts of

SO_4-S to the humus horizons – in rendzinas from 12.5 to 26.9 mg · kg^{-1}, and in soils lessives from 9.1 to 67.5 mg · kg^{-1}. The decisive role as a barrier in sulphate sulfur transport into the deeper parts of the soil profile have the humus-rich surface horizons, what was reported in previous studies as well [16]. There were no statistically significant differences in the sulfur content between the corresponding horizons of soils lessives and rendzinas.

The accumulation of sulfur in humus horizons was statistically dependent on total nitrogen content (r_s = 0.6410, p = 0.001) and organic carbon content (r_s = 0.4454, p = 0.05) (Fig. 2). Similar correlation was found in soils of the Tatra National Park [15].

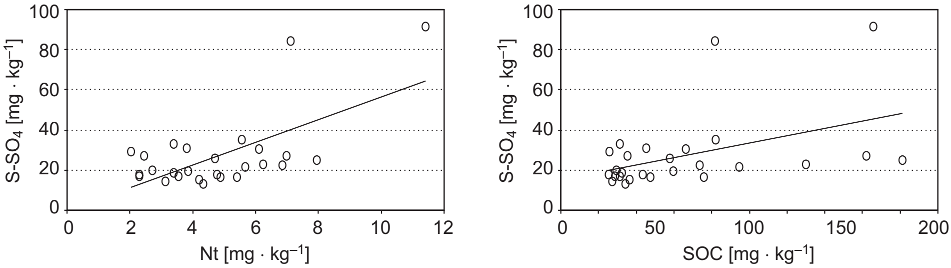

Fig. 2. Sulphur content related to total nitrogen content – Nt (r_s = 0.6410, p = 0.001) and organic carbon content – SOC (r_s = 0.4454, p = 0.05)

Calculated accumulation index (AI) values for the organic Ol horizons were significantly higher than the values determined for corresponding humus horizons. The values of AI for rendzinas and soils lessives were similar (Fig. 3).

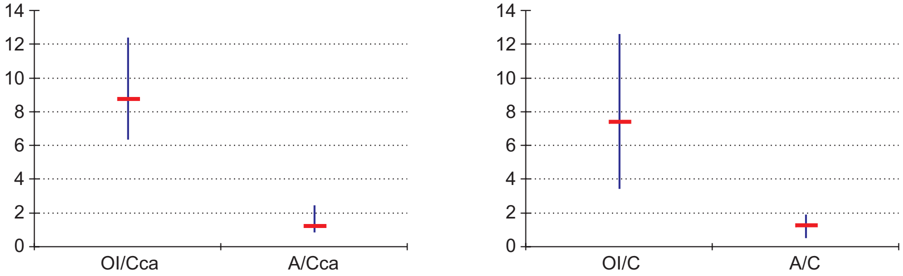

Fig. 3. Accumulation index (AI) calculated for investigated rendzinas (above) and soils lessives (below)

Sulphate sulfur content in soils was conditioned by the location of soils. The highest amounts of SO_4-S in organic horizons were found in soils located within the Pradnik Valley, in the section of the Ojcow – Pradnik Korzkiewski. However, the largest values of SO_4-S in humus horizons were determined in soils of Wola Kalinowska village (Fig. 4).

The pedogenesis direction in soils lessives had no effect on the profile distribution of sulfur. Concentration of SO_4-S did not vary significant between eluvial (Et) and illuvial horizons (Bt), and ranged from 15.9 to 47.3 mg · kg^{-1} and from 12.3 to 49.8 mg · kg^{-1},

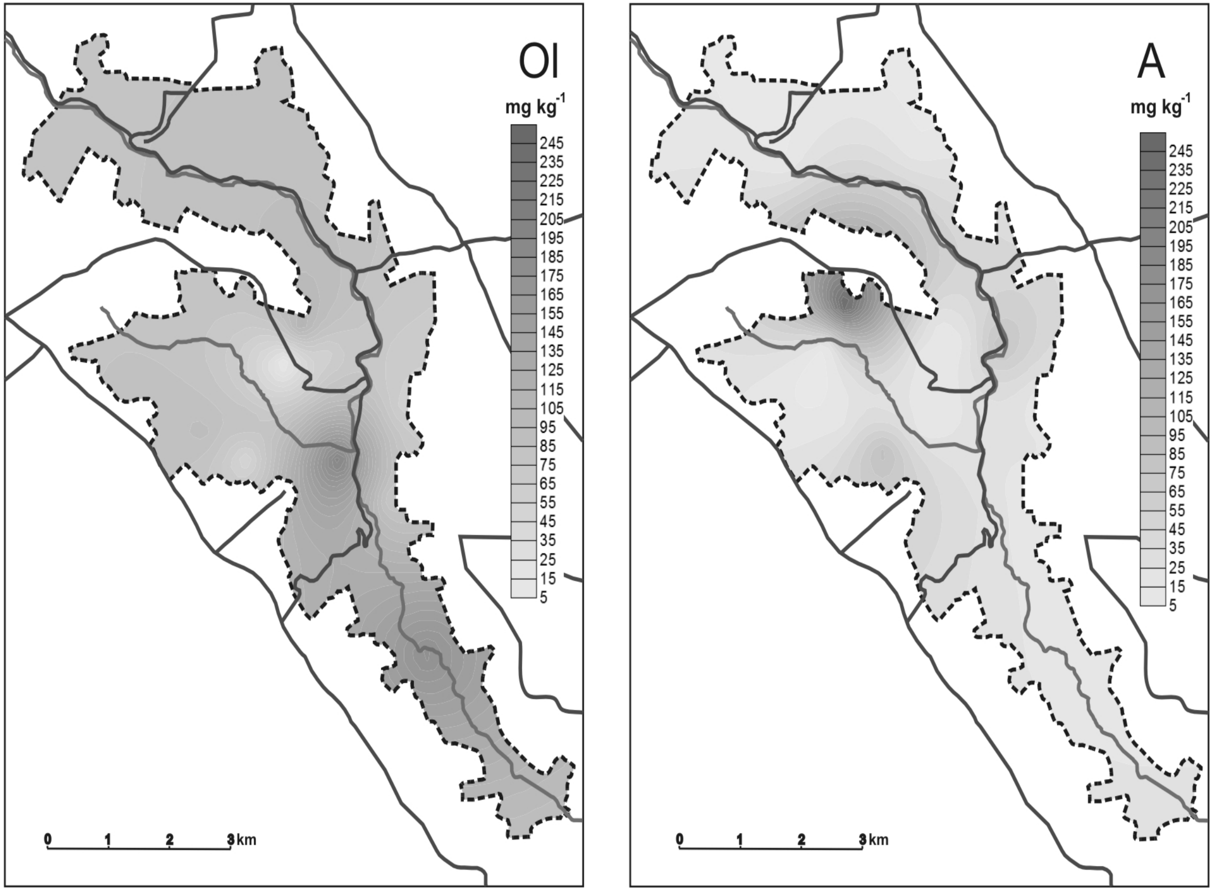

Fig. 4. Sulphur content [mg · kg^{-1}] in organic (Ol) and humus (A) horizons of studied soils

respectively (Fig. 5). Differences in content of SO_4-S in genetic horizons are similar in all studied rendzinas profiles (Fig. 5). Profile distribution of sulphur in rendzinas was similar to soils lessives. Determined sulfur content in profiles of soils lessives and rendzinas was dependent mainly on the humus accumulation process [16].

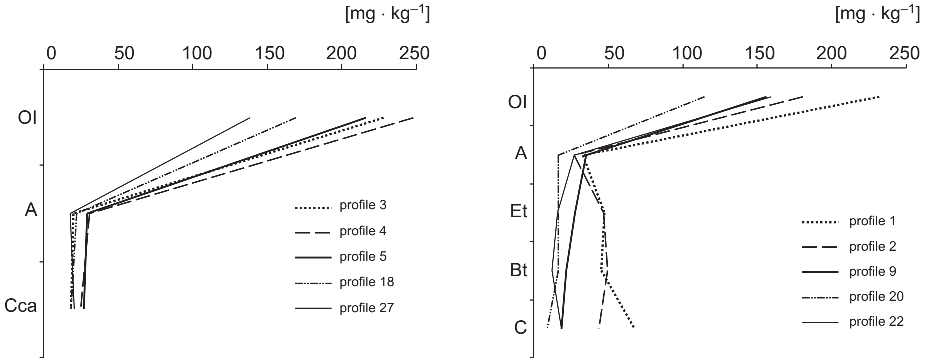

Fig. 5. Profile distribution of sulphur in chosen rendzinas (above) and soils lessives (below)

Therefore, there was no evident effect of soil direction development on the content of sulphate sulfur, what was previously reported by Skłodowski [9] in the soils lessives and by Zadrożny and Miechowka [15] in podzols. The high variability of relief and diversity within a soil type unit was the reason.

Moreover, the content of the analyzed component was determined primarily by the specific terrain relief and secondary by the geographical location of soils. The amount of deposited in soil air pollutants containing sulfur compounds was determined also by local climate conditions, which vary greatly on the area of the Ojcow National Park [4, 13, 17].

Conclusions

1. The highest content of sulphate sulfur in soils of the Ojcow National Park was determined in organic Ol horizons.
2. There were no significant differences in sulphate sulfur content, profile distribution and accumulation indices between soils lessives and rendzinas.
3. Organic horizons of soils located in the Pradnik Valley, within the section Ojcow – Pradnik Korzkiewski, were characterized by a highest content of SO_4-S. The highest content of sulphur in humus horizons was determined in soils of the area of Wola Kalinowska village.

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SIARKA W GLEBACH LEŚNYCH OJCOWSKIEGO PARKU NARODOWEGO

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Abstrakt: Celem pracy było określenie wpływu kierunku pedogenezy na zawartość siarki w glebach leśnych Ojcowskiego Parku Narodowego (OPN). Badaniami objęto gleby reprezentujące główne jednostki pokrywy glebowej OPN: rędziny brunatne i gleby płowe. Badane gleby charakteryzowały się dużą zmiennością zawartości siarki siarczanowej w obrębie profilu. Największe ilości S-SO$_4$ zawierały powierzchniowe poziomy organiczne Ol (rędziny 104,2–248,0 mg · kg^{-1}, gleby płowe 101,0–232,0 mg · kg^{-1}). W poziomach próchnicznych A zawartość siarki była niższa (rędziny 14,1–91,4 mg · kg^{-1}, gleby płowe 16,5–35,5 mg · kg^{-1}) i zbliżona do wartości w poziomach spągowych analizowanych profilów (rędziny 12,5–26,9 mg · kg^{-1}, gleby płowe 9,1–67,5 mg · kg^{-1}). W glebach płowych stwierdzono małe zróżnicowanie pomiędzy poziomami eluwialnymi (Et, 15,9–47,3 mg · kg^{-1}) a iluwialnymi (Bt, 12,3–49,8 mg · kg^{-1}).W badanych glebach nie stwierdzono wpływu kierunku pedogenezy i ich rozwoju na zawartość siarki siarczanowej. Było to prawdopodobnie spowodowane dużą zmiennością rzeźby i zróżnicowaniem badanych profilów w obrębie danego typu. Ponadto wydaje się zasadne stwierdzenie, że zawartość analizowanego składnika była najbardziej determinowana specyfiką ukształtowania terenu i położeniem geograficznym badanych gleb.

Słowa kluczowe: siarka, gleby, Ojcowski Park Narodowy

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Katarzyna SOŁEK-PODWIKA[1]

SOIL ENZYMATIC ACTIVITY IN THE IMPACT ZONE OF SULPHUR COMPOUNDS EMISSION

AKTYWNOŚĆ ENZYMATYCZNA GLEB W STREFIE ODDZIAŁYWANIA EMISJI ZWIĄZKÓW SIARKI

Abstract: Activity of various enzymes is used for the assessing the effect of anthropogenic fsctors on soil microbiological activity. Dehydrogenase activity is considered a measurement of total soil microbiological activity. A crucial element of anthropogenic transformations of the natural environment is acid soil degradation caused by the storage of acid forming substances, such as *eg* elementary sulphur and atmospheric pollution with its compounds. In Poland the largest areas strongly polluted with sulphur are situated in the Tarnobrzeg Sulphur Basin, where pulverized sulphur (transported by wind from the minefields and places of storage) and the products of its oxidation, such as acid rains or dry deposit have found its way not only to the soils covering the mining area but also to the soils beyond the boundary of the mine area.

The research aimed to assess the influence of pollution emitted during the thirty-year-long exploitation of sulphur deposits on the microbiological activity of soils situated in the vicinity of "Grzybow" Sulphur Mine.

The investigated soils taken from the areas situated in neighbouring of mine are characterized by low, as a rule below 1, level of degydrogenase activity and acid soil reaction and generally a high share of sulphate sulphur in the total sulphur content. The conducted assessment of the activity of studied enzymes shows, that the pollution of the soil environment around the mine remains on the level which may pose a threat to living organisms. The cause of the considerable decrease of the level of dehydrogenase activity of studied soils may be their acid reaction which is the result of long-term emission of sulphur compounds. In the surface soil layer sulphur is oxidized to sulphuric acid, which cause a strong soil acidification.

Keywords: dehydrogenase activity, acid soils, sulphur mine

Activity of various enzymes is used for determining the effect of anthropogenic factors on soil microbiological activity [1, 2]. Dehydrogenase activity is considered a measure of total microbiological activity in soils and it is often determined in order to assess the soil anthropogenic transformations. A crucial element of anthropogenic transformations of the natural environment is acid soil degradation caused by the storage of acid forming substances, such as *eg* elementary sulphur and atmospheric pollution with its compounds. In Poland the largest areas strongly polluted with sulphur

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are situated in the Tarnobrzeg Sulphur Basin, where extraction and processing of sulphur have led to a considerable pollution of the atmosphere, soils, surface and underground waters. Pulverized sulphur (transported by wind from the minefields and places of storage) and the products of its oxidation, such as acid rains or dry deposit have found its way not only to the soils covering the mining area but also to the soils beyond the boundary of the mine area. In the soil surface layer sulphur is oxidized to sulphuric acid, which causes strong soil acidification [3–5].

The research aimed to assess the influence of pollution emitted during the thirty-year-long exploitation of sulphur deposits on the microbiological activity of soils situated in the vicinity of "Grzybow" Sulphur Mine.

Materials and methods

The material for analyses was collected from mineral surface and subsurface horizons of 9 representative surfaces located about 3 km from the boundaries of the former "Grzybow" sulphur mine, which was the first mine in Poland as well in Europe where sulphur deposits were exploited using the borehole Frash method. Later, exploitation with the borehole Frash method was also led on areas of mines "Jeziorko", "Osiek" and "Basznia". Although the method of underground smelting of sulphur was regarded less harmful to the environment than an opencast mining, geochemical, hydrological and chemical transformations are spread through not only areas where mining works were led but also on areas occurring beyond borders of mine. The cause of chemical transformations (acidity) of these areas was a significant degree of the atmospheric air pollution by sulphur compounds entering different components of ecosystems. As Levyk and Brzezinska [5] say mining activity within Roztocze region contributed to impoverishment of the species, landscape and ecosystems diversities. Soils of areas beyond the border of Sulphur Mine "Grzybow", in contrast with the soil of mining fields weren't subjected to reclamation treatments aiming at an improvement of their physical and chemical properties.

On selected surfaces (wastelands, overgrown with grasses) remaining under impact of long-lasting emission of sulphur compounds field research was carried on during which soil was sampled for laboratory analyses,

In air dried soil material pH in H_2O and in 1 mol · dm^{-3} KCl solution was estimated potentiometrically, soil texture using the Casagrande areometric method in Proszynski's modification, organic C content by means of the Tiurin method modified by Oleksynowa, total N using the Kjeldahl method and total S and $S\text{-}SO_4$ using the modified Barsley-Lancaster methods [6]. Sulphur forms were determined in the obtained extracts using the gravimetric method according to Polish standards PN-75 C-04566/21 and PN-74 C-04566/09. The soil dehydrogenase activity was assessed by colorimeter after 24 hour incubation of the soil samples at 37 ^{o}C with TTC solution (2,3,5-Triphenyltetrazolium Chloride) used a substrate for measuring the investigated enzymes with the Casidy et al [7] method and stated in cubic centimeters of hydrogen per 1 kilogram of soil per day [$cm^3H_2 \cdot kg^{-1} \cdot d^{-1}$].The intensity of colouration was measured using the Beckman DU 600 spectrophotometer at the wavelength 485 nm.

Considering seasonal changes of the enzymatic activity samples of the soil for estimating the dehydrogenase activity were taken twice a year: in May and October, from both depths of every surface. Values of the dehydrogenase activity, presented in the paper, in the soil of the given surface are mean values from estimations in the spring and autumn terms.

Results and discussion

Sulphur is ranked among elements widely spread in the biosphere, the nutrients essential for the normal growth and the development of plants. It is also one of pollutants occurring most often which are contributing to the ground acidity, the same constituting a considerable risk for the balance of the entire ecosystem [4]. A considerable diversification of the assessed sulphur compound content was found in the analyzed soils (Table 1).

Table 1

Selected physicochemical properties of analysed soils

Profile No.	Depth [cm]	pH		C_{org}	N_{tot}	S_{tot}	$S\text{-}SO_4$	< 0.02 [%]
		H_2O	KCl	$[g \cdot kg^{-1}]$				
1	0–18	4.92	3.75	13.85	1.20	0.129	0.002	6
	18–32	5.33	4.19	7.44	0.84	0.113	0.003	7
2	0–17	4.72	3.59	70.36	5.80	0.893	0.015	9
	17–33	4.75	3.74	25.92	2.27	0.215	0.006	9
3	0–24	4.35	3.25	6.12	0.65	0.046	0.003	5
	24–41	5.09	3.65	0.69	0.11	0.010	0.006	5
4	0–25	6.31	5.25	11.23	2.09	0.144	0.015	8
	25–42	5.89	4.72	11.49	0.77	0.022	0.012	8
5	0–20	5.21	4.51	15.15	2.20	0.223	0.018	24
	20–35	5.44	4.47	5.82	0.97	0.071	0.015	22
6	0–16	4.70	3.91	11.22	1.03	0.129	0.008	26
	16–29	4.77	3.98	9.37	1.02	0.105	0.009	28
7	0–22	5.92	5.13	7.68	0.95	0.127	0.005	8
	22–35	5.21	4.16	0.54	0.22	0.044	0.010	3
8	0–28	4.86	3.71	4.10	0.64	0.036	0.007	5
	28–41	4.85	4.02	1.57	0.23	0.020	0.006	3
9	0–23	4.72	3.55	5.57	0.65	0.049	0.011	6
	23–33	4.61	3.45	0.51	0.25	0.045	0.014	4

S_{tot} content fell within the range from 0.01 to 0.893 $g \cdot kg^{-1}$ of soil and was diminishing with the soil depth. The assessed content of S-total was approximate to the quantities of this element in the mineral soils of Poland [8]. Apart from the total sulphur also sulphate sulphur was assessed in the analysed soils (Table 1). Their amount indicates a hazard posed to the soil environment by this element excessive emission due to anthropopressure. The share of $S\text{-}SO_4$ in the total sulphur content in the mineral soils of Poland does not exceed 10 % and higher concentrations are considered the result of anthropopressure [8]. In the surface horizons of the analysed soils the percentage share of sulphate sulphur in the total sulphur content was the lowest (it did not as a rule exceed 10 %) and was increasing with depth, reaching even 60 % (Fig. 1) in the subsurface horizons. In view of limited inflow of elementary sulphur pollutants (due to the mine close-down) to the soils of the investigated area, it was mainly caused by sulphate translocation from surface horizons to lower situated ones. On the basis of limit numbers of total sulphur and sulphate sulphur content in the soil surface horizons suggested by IUNG [8], the researched soil with texture of loamy sands and light loams were counted among the soils with natural content of the analysed sulphur forms.

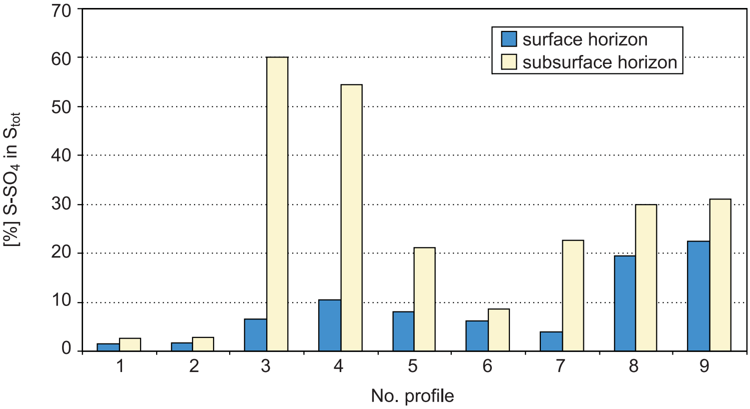

Fig. 1. Participation of $S\text{-}SO_4$ [%] in S_{tot} content

Dehydrogenase activity in the surface horizons of the studied soils ranged between 0.13 and 1.85 $cm^3H_2 \cdot kg^{-1} \cdot d^{-1}$ and was decreasing with increasing soil depth (in the subsurface horizons it fluctuated from 0.11 to 0.28 $cm^3H_2 \cdot kg^{-1} \cdot d^{-1}$, Fig. 2). On the basis of many experiences a diversified level of the dehydrogenase activity depending on the depth of the soil profile was stated. Their activity achieves the maximum values in top horizons, and along with the increase in the depth of the soil profile, a decline in the activity of these enzymes is observed [9].

According to Bielinska et al [10] such regularity is mainly connected also with the profile distribution of humus in soil. Higher values of the analyzed enzymes in the surface horizons of the analyzed soils were accompanied by higher values of organic C. In the surface horizons the range of organic carbon content was from 4.10 to 70.36 $g \cdot kg^{-1}$ of soil and in the subsurface horizons between 0.54 and 25.92 $g \cdot kg^{-1}$ of soil. However, statistical analysis conducted on the obtained results did not reveal any significant dependency between the assessed enzymatic activity and the content of total

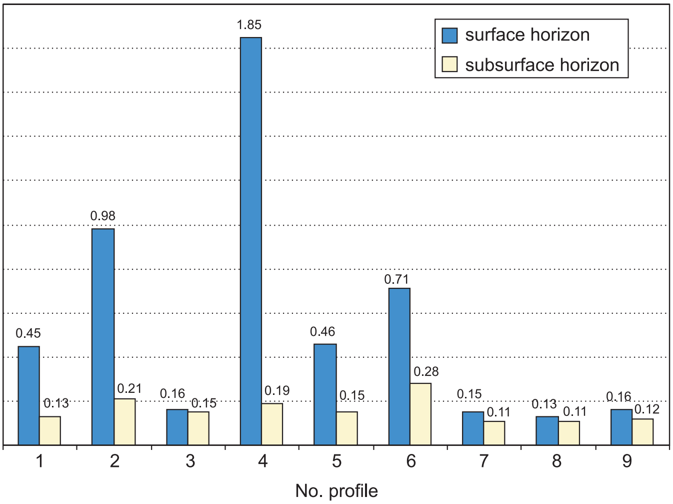

Fig. 2. Level of dehydrogenase activity in horizons of analysed soils [$cm^3H_2 \cdot kg^{-1} \cdot d^{-1}$]

nitrogen, organic carbon and sulphur compounds. Levyk and co-authors [9] stated the lack of the statistical relation between the dehydrogenase activity and the degree of the sulphur content, examining the activity of these enzymes in the chemically degraded soils, located soil in areas of the sulphur mine of Jaworow and Nemyriv (Ukraine).

The obtained results of deydrogenase activity (Table 1) point to high inactivation of the studied enzymes in the soils collected from the areas situated in the vicinity of former Grzybow sulphur mine. Similar values of dehydrogenase activity (below one) were also assessed by Bielinska et al [10–12] while determining these enzymes activity in the soils of the industrialized city agglomerations of the upper Silesia and in the soils transformed as a result of the mining operation of the sulphur mine in Piaseczno, but also in the soil which for a long time remained under nitrogen emission, situated in the immediate neighbourhood of the Pulawy S. A. fertilizer factory. According to Bielinska et al [10, 11] low dehydrogenase activity in soils evidences a lowered Total Microbiological Activity (TMA) of the environment and its cause in the investigated soils may be their reaction.

It is one of the crucial soil features which is an important factor of their productivity because it directly affects the development of microorganisms and higher plants. Martyn et al [3] state that pH value in KCl ranging from 4.6 to 5.0 in the surface horizons of soils located in the vicinity of sulphur mines points to a negative effect of sulphur extraction and storage. The main reason for this might be spreading sulphur dust throughout the neighbourhood by wind and precipitations. The investigated soils situated under many-year influence of Grzybow borehole sulphur mine revealed pH values within the range from 3.25 to 4.75 and on this basis they were counted among acid and very acid soils, except the subsurface horizon of the profile 4 soil where pH value in KCl was the highest 5.25. The soil of this horizon was also characterised by the highest activity of the investigated enzymes – 1.85 $cm^3H_2 \cdot kg^{-1} \cdot d^{-1}$, which corroborates the results obtained by Frankenberger and Johanson [13], who on the basis of conducted research found that even small changes of pH values may considerably change the activity of soil enzymes. The influence of the soil reaction on the enzymatic activity was noted also by Levyk and collaborators [9] when comparing the dehydrogenase activity of the anthropogenic soil transformed as a result of the exploitation of sulphur deposits. On the basis of conducted estimations authors stated several times lower the level of the activity of examined enzymes in acid soils than in alkaline ones. According to many authors, the most beneficial reaction conditions for the activity of dehydrogenases are close to neutral [14, 15].

Conclusions

1. Many-year extraction and storage of sulphur in the area of "Grzybow" Sulphur Mine had a negative influence on the state of the natural environment of the neighbouring areas including the analysed soils. These soils are characterized by a low, as a rule below one, level of soil dehydrogenase activity and acid reaction, and a generally high share of sulphate sulphur in total sulphur content.
2. The cause of the considerable decrease of the level of dehydrogenase activity of studied soils may be their acid reaction which is the result of long-term emission of sulphur compounds.

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AKTYWNOŚĆ ENZYMATYCZNA GLEB W STREFIE ODDZIAŁYWANIA EMISJI ZWIĄZKÓW SIARKI

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Abstrakt: Aktywność różnych enzymów wykorzystuje się do oszacowania wpływu antropogenicznych czynników stresowych na aktywność mikrobiologiczną gleb. Za miarę całkowitej aktywności mikrobiologicznej w glebie uznaje się aktywność dehydrogenaz, których oznaczenie jest często stosowane jako ocena stopnia antropogenicznych przekształceń gleb. Istotnym elementem antropogenicznych przekształceń środowiska przyrodniczego jest kwasowa degradacja gleb, której przyczyną jest składowanie kwasotwórczych substancji, np. siarki elementarnej i zanieczyszczenie atmosfery jej związkami. W Polsce największe obszary gleb silnie zasiarczonych występują w Tarnobrzeskim Zagłębiu Siarkowym, gdzie rozpylona siarka (transportowana eolicznie z pól górniczych i miejsc składowania) oraz produkty jej utlenienia w postaci kwaśnych deszczy lub suchego opadu dostawała się nie tylko do gleb położonych na terenie kopalń, ale także do gleb znajdujących się poza ich granicami.

Celem badań była ocena wpływu zanieczyszczeń emitowanych podczas 30-letniej eksploatacji złóż siarki na aktywność mikrobiologiczną gleb położonych w sąsiedztwie Kopalni Siarki Grzybów. Badane gleby, pobrane z terenów położonych w sąsiedztwie kopalni charakteryzują się niskim, z reguły poniżej jedności, poziomem aktywności dehydrogenaz glebowych oraz kwaśnym odczynem i z reguły wysokim udziałem siarki siarczanowej w zawartości siarki ogółem. Aktywność dehydrogenaz w poziomach powierzchniowych badanych gleb mieściła się w granicach od 0,13 do 1,85 $cm^3H_2 \cdot kg^{-1} \cdot d^{-1}$ i zmniejszała się wraz ze wzrostem głębokości gleby (w poziomach podpowierzchniowych kształtowała się w zakresie od 0,11 do 0,28 $cm^3H_2 \cdot kg^{-1} \cdot d^{-1}$). Przeprowadzone oznaczenia aktywności badanych enzymów wskazują, że wielkość zanieczyszczenia środowiska glebowego wokół kopalni pozostaje na poziomie, który może zagrażać organizmom żywym. Przyczyną znacznego obniżenia poziomu aktywności dehydrogenaz badanych gleb może być ich kwaśny odczyn, który jest wynikiem długoletnich emisji związków siarki. Siarka w powierzchniowej warstwie gleby ulega utlenieniu do kwasu siarkowego, który powoduje silne zakwaszenie gleb. Badane gleby znajdujące się w zasięgu długoletniego oddziaływania otworowej kopalni siarki Grzybów charakteryzowały się wartościami pH w KCl w zakresie od 3,25 do 4,75 i na tej podstawie zostały zaliczone do gleb kwaśnych i bardzo kwaśnych.

Słowa kluczowe: aktywność dehydrogenaz, gleby kwaśne, kopalnia siarki

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EFFECT OF SAPONIN EXTRACT ON VERMICOMPOSTING OF SELECTED ORGANIC WASTE

WPŁYW EKSTRAKTU SAPONINOWEGO NA WERMIKOMPOSTOWANIE WYBRANYCH ODPADÓW ORGANICZNYCH

Abstract: Vermicomposting of livestock manure and organic kitchen refuse is a possible way of utilizing this type of waste. The study was designed to assess the impact of saponin extract on the characteristics of the earthworm *Eisenia fetida* used for vermicomposting of swine manure with added organic kitchen refuse and cellulose, as well as its effect on the chemical composition of the produced vermicomposts. During the study, extract of *Quillaja saponaria* added to the waste did not affect the size and mass of the population or reproduction of the earthworms, yet it adversely modified the mass of adult specimens. The vermicomposts obtained had varied composition. Significant differences were shown in the contents of sodium, calcium, copper and zinc.

Keywords: swine manure, organic kitchen refuse, cellulose, *Eisenia fetida* (Sav.), saponins, vermicompost

Introduction

An increasing volume of municipal waste, including organic kitchen refuse, generated in rural areas is not utilized or processed, which is directly linked with a change in lifestyle leading to greater consumption of goods. In addition to organic kitchen waste, the volume and quality of biomass wastes produced in rural areas are connected with crop and animal production. At present, livestock farming is a particularly expansive type of agricultural operation leading to production of such waste as farmyard manure, slurry, urine manure, and poultry droppings. All these types of waste inadequately utilized can pose hazards for the environment; alternatively they are a valuable source of nutrients for crops.

Highly concentrated pig farming leads to excessive size of stock in relation to the area designated for plant production and is the reason why animal manure is

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increasingly burdensome for the surroundings [1]. This is caused by ammonia, which is produced during decomposition of nitrogen compounds contained in excrements, and is harmful for people, animals and the natural environment. It is estimated that livestock farming is responsible for approximately 50 % of global ammonia emissions. Penetrating the soil along with rainwater, ammonia adversely affects the nitrogen balance leading to changes in natural ecosystems and agrocoenoses. Excessive amounts of ammonia derivatives causes deactivation of biological life in specific components of the environment, which then leads to a loss in its capacity for self-purification and gradual degradation [2–6].

Methods of reducing ammonia emissions from animal excrements, which have been used for years, include the use of deodorizing agents (*eg* microbiological, humic and chemical). Due to the fact that synthetic agents frequently cause allergic reactions in animals, increasingly popular are formulas containing saponin substances obtained from extract of such plants as *Yucca schidigera* and *Quillaja saponaria*.

Most saponin substances show strong biotic activity. For instance saponins promote growth of beneficial microflora in the digestive system of animals and hinder activity of urease, the enzyme which is responsible for disintegration of urea into ammonia [7–9].

Supplementing livestock fodder with saponin agents contributes to reduced ammonia emission in the animals' immediate surroundings, and as a result improves their productivity and health [10]. Because of their natural origin, saponin agents secreted into the environment with excrements should biodegrade. Yet, no research has been conducted to investigate their impact on biological diversity, including soil macrofauna and earthworms, as significant elements of trophic chains.

Earthworms, commonly occurring in various types of soil, are not only good bioindicators showing the state of the environment (they are used in monitoring of the soil environment because they come into contact with soil *via* their skin and, internally, through their digestive system) [11], but they are also used in organic waste utilization and vermicompost production [12, 13].

Numerous studies [14–18] have shown evidence that vermicomposting can be applied to kitchen refuse, as well as waste generated by paper plants, distilleries and other types of industry.

The purpose of the study was to assess the impact of saponin extract on the characteristics of earthworms used in the vermicomposting process, based on swine manure with added organic kitchen waste and cellulose as well as the effect on chemical composition of the vermicompost obtained.

Materials and methods

The experiment was conducted in plastic containers with the capacity of 3 dm^3, filled with selected organic waste (swine manure, kitchen refuse and cellulose, in the proportion of 1:1:1 calculated per dry mass). The process of vermicomposting was conducted with earthworms of the species *Eisenia fetida* (Sav.) following the pattern shown in Table 1.

Table 1

Pattern of the experiment

Specification	Container no. (replication)	Waste used in vermicomposting process	Initial number and total mass of the earthworm population per container
Control group (C)	1–3	250 g of swine manure + 250 g* organic kitchen refuse + 250 g of cellulose**	20 sexually mature specimens of *E. fetida* with the assessed total biomass of 9.279 ± 0.110 g
Experimental group (E)	4–6	250 g of swine manure + 250 g* organic kitchen refuse + 250 g of cellulose** + saponin extract	20 sexually mature specimens of *E. fetida* with the assessed total biomass of 9.304 ± 0.208 g

* Pasta leftovers, apple and potato peelings, at the ratio of 1:1:1; ** waste cardboard egg box.

The substrate used in the vermicomposting process in the experimental group (D) was supplemented with saponin extract from *Quillaja saponaria* amounting to 0.125 mg per container. The amount of saponin extract used as a supplement was similar to the extract dosage administered with fodder in pig farming.

The experiment was conducted in laboratory conditions, during March–April 2012 (air temperature 20 ± 5 ^{o}C). Changes in the characteristics of the study populations of earthworms (number, and body mass in specimens of specific age groups and cocoons) were checked every three weeks. The earthworms were detected by means of manual segregation of the substrates subjected to the process of vermicomposting. The detected specimens and cocoons produced by them were counted and weighed.

The contents of selected elements (C, N, P, K, Ca, Na, Mg, Fe, Mn, Zn, Cu and Pb) in the vermicompost were determined in the Faculty Laboratory for the Analysis of Environment Health and Materials of Agricultural Origin, at the University of Rzeszow. The contents of C and N were identified by means of Vario El-Cube elemental analyzer manufactured by Elementar. Samples of vermicomposts were digested in *aqua regia* using Berghof Speed Wave Four microwave digestion system. The contents of macro- and microelements were identified using a Hitachi Z-2000 series atomic absorption spectrophotometer. The total phosphorus contents were measured by means of vanadium-molybdenum method using Jasco V-530.

The findings of the experiment were analyzed using Microsoft Office Excel 2007 spreadsheet and presented as mean values ($\overline{x}$) for experiments replicated three times and as standard deviation (*SD*). The results were tested using one-way analysis of variance, and the significance of differences between arithmetic means was estimated with Tukey's test (α = 0.05); for this purpose Statistica PL software was used.

Results and discussion

Authors' own findings suggest that saponin extract of *Quillaja saponaria* added to organic waste used in the vermicomposting process did not affect the size and mass of the earthworm (*E. fetida*) population participating in this biotechnology (Table 2, Fig. 1).

Table 2

Characteristics of earthworm *E. fetida* populations used in the vermicomposting process utilizing the prepared mixtures

Group	Total population		Mature individuals		Immature individuals		Cocoons	
	number [ind. ± SD]	total biomass [g ± SD]	number [ind. ± SD]	total biomass [g ± SD]	number [ind. ± SD]	total biomass [g ± SD]	number [ind. ± SD]	total biomass [g ± SD]
Control (C)	72 ±36	18.339 ±9.361	28 ±12	14.506 ±6.363	44 ±14	5.117 ±4.185	58 ±32	0.689 ±0.333
Experi-mental (E)	70 ±31	14.678 ±5.785	24 ±9	11.005 ±4.403	47 ±18	4.927 ±2.881	61 ±31	0.737 ±0.339

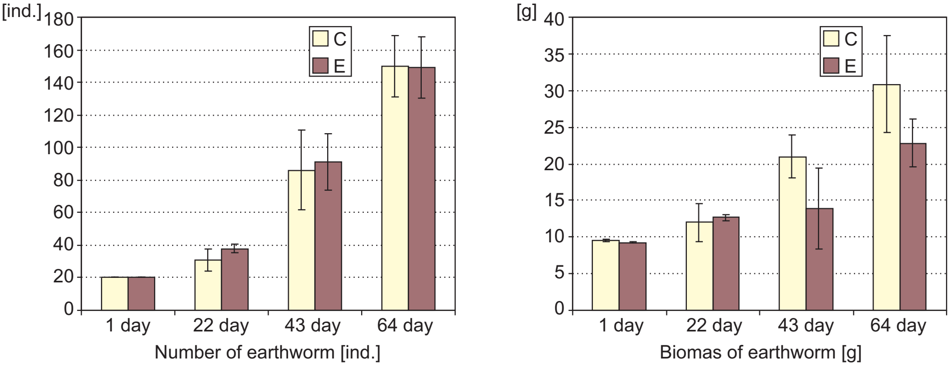

Fig. 1. Dynamics of the changing number and biomass of earthworm in the populations during the period of the experiment (ind. ± SD); C – control; E – experimental group

Although the size and mass of earthworm populations were slightly higher in the control group, the identified differences were not significantly statistically different. Statistically significant differences were found when mean masses of mature specimens were compared throughout the entire duration of the experiment (Table 3). The experimental specimens were smaller than the controls.

Table 3

Individual mass of *E. fetida* in age groups and mass of cocoons – mean values for all measurements (mean ± SD)

Group	Mature specimens	Immature specimens	Cocoons
	[g]		
Control (C)	0.516* ± 0.041	0.086 ± 0.035	0.012 ± 0.001
Experimental (E)	0.485* ± 0.077	0.083 ± 0.036	0.013 ± 0.002

* Differences statistically significant at α = 0.05.

During the time of experiment, the presence of saponin extract in the mixed waste participating in the vermicomposting process did not significantly alter reproduction of the populations (Tables 2 and 3), although the number and mass of cocoons produced in the substrate supplemented with saponins were slightly higher. This may have been caused by a modified life strategy adopted by the more actively reproducing population staying in the substrates with saponins and the resulting greater loss of mass in the earthworms multiplying in slightly higher numbers in the experimental containers.

The experiment made it possible to successfully utilize biodegradable waste mixed at the ratio of 1:1:1, *ie*: swine manure (code 02 01 06), selected organic kitchen refuse (20 01 08) and waste cellulose (03 03 08), whose improper storage and utilization may lead not only to loss of fertilizing components but also to hazards such as spreading diseases and pollution of ground water and air.

According to projections included in the National Waste Management Plan 2014 (KPGO) [19], the amount of waste generated by agriculture, fruit farming and hydroponic crops and other biodegradable waste other than municipal waste classified in group 02, will increase from 6,052 thousand Mg in 2011 to 6900 thousand Mg in 2022. In the case of municipal organic waste KPGO predicts an increase from 6,088 thousand Mg in 2011 to 7,761 thousand Mg in 2022. An equally significant increase is expected for cellulose pulp, as a component of the group of waste with 03 code, which will grow from 3,028 thousand Mg to 3,444 thousand Mg in the period from 2011 to 2022.

Monitoring of existing waste management in rural areas, particularly related to municipal waste, including biodegradable waste (code 20 01), shows that the situation is becoming similar to that existing in urban areas.

In accordance with the objectives envisaged by KPGO (2014) (* provide organized municipal waste collection schemes for 100 % of the population by 2015, at the latest; ** ensure that services under selective waste collection schemes are provided to all inhabitants by 2015, at the latest; *** reduce quantities of municipal biodegradable waste deposited at landfills, so that by 2013 the amount of waste deposited at landfills does not exceed 50 % and by 2020 it is no more than 35 % of the volume of waste generated this way in 1995), the long-term road towards the strategy for building a national waste management system is equivalent to achieving compliance with the principles of sustainability.

Similar objectives are imposed on decision makers and citizens by the current Act on waste, which strictly implements the EU directive 2008/98/EC on waste. The Act of 14 December 2012 on waste [20] replaces the previously binding Act of 27 April 2001 on waste (consolidated text: Journal of Laws, 2010, No 185, item 1243, as amended) and became effective on 23 January 2013.

Recycling and organic recycling are very significant components of sustainable waste management systems. Organic recycling is understood as treatment of biodegradable waste by means of aerobic (*eg* composting) or anaerobic (fermentation) processes conducted in controlled conditions using microorganisms. As a result of composting one can obtain fertilizers which have significant content of crop nutrients and are currently in high demand. Approval of composts for commercial use is strictly regulated by applicable laws.

Trends and perspectives for municipal waste composting systems have been discussed *eg* by Goscinski [21], who described both simple compost heaps located on the ground and complex bioreactors utilizing municipal waste in large cities. Potential applications and the importance of vermicomposting to be used for biodegradable waste treatment under community waste management programmes have been outlined by Kasprzak [22] and Bozym [23] while other studies have demonstrated that vermicomposting is an effective method of neutralizing both farmyard manure [24–26], organic kitchen refuse [27, 28] and cellulose [13, 15].

It should be emphasized that the process of neutralization carried out for 64 days using quantities described in the methodology, where swine manure was supplemented with kitchen refuse and cellulose, was successful both in the control group and in the containers with added contents of saponin extract. The vermicomposts produced had visibly different organoleptic properties; unlike the input material they had uniform crumb structure, dark colour, and had no unpleasant smell.

Chemical composition of vermicomposts based on mixtures of selected organic materials with and without saponin extract is shown in Table 4.

Table 4

The content of selected elements in vermicomposts produced (mean ± SD)

Specification		Vermicomposts	
		Control (C)	With saponin extract (E)
Carbon	$[g \cdot kg^{-1}]$	241.9 ± 30.1	279.7 ± 22.8
Nitrogen		71.524 ± 14.322	75.322 ± 15.834
Phosphorus		2.150 ± 0.487	2.151 ± 0.850
Potassium	$[mg \cdot g^{-1}]$	3.107 ± 0.517	3.707 ± 0.323
Sodium		0.384* ± 0.094	0.220* ± 0.085
Calcium		47.214* ± 2.899	38.783* ± 2.608
Magnesium		1.669 ± 0.181	1.471 ± 0.117
Iron		13.526 ± 1.692	13.770 ± 1.411
Copper		0.025* ± 0.004	0.015* ± 0.001
Zinc		0.036* ± 0.004	0.028* ± 0.002
Manganese		0.263 ± 0.020	0.266 ± 0.015
Lead		0.018 ± 0.002	0.016 ± 0.008

* Differences statistically significant at $\alpha = 0.05$.

The most pronounced differences between these vermicomposts were found in the content of calcium ($8.43\ mg \cdot g^{-1}$ ± 5.57), sodium ($0.16\ mg \cdot g^{-1}$ ± 0.04), copper ($0.01\ mg \cdot g^{-1}$ ± 0.004) and zinc ($0.008\ mg \cdot g^{-1}$ ± 0.005). They were confirmed statistically ($p \leq 0.05$). In the case of the remaining mineral elements the differences between the experimental and control group were much smaller and statistically insignificant.

Kostecka and Paczka [29] conducted another experiment in which the same mixture of organic kitchen refuse was used and the chemical composition of the vermicomposts differed depending on the applied technology of vermicomposting. Significantly higher contents of nitrate nitrogen NO_3-N (differences of value 558 g · dm^{-3}), assimilable phosphorus (of 195 g · dm^{-3}), potassium (of 710 g · dm^{-3}), magnesium (of 170 g · dm^{-3}) and calcium (of 166 g · dm^{-3}) were found when, in accordance with the applied technology, the substrate and the earthworm populations were not frequently divided. On the other hand the method based on frequent division of the substrate and earthworm populations promoted reduction of NaCl contents in vermicompost.

Vermicomposts obtained by Kostecka and Kolodziej [25], based on cattle manure had extremely high contents of nutrients. In that case the vermicomposting process contributed to increased contents of nitrogen and total phosphorus, in comparison with their average contents observed in cattle manure. By contrast, Gasior et al [24] reported that the contents of most elements in vermicompost based on swine manure was similar to those found in cattle and sheep manure vermicomposts.

As a conclusion, taking into account other studies [30–32], it can be assumed that products of vermicomposting process are characterized by high contents of nitrogen and other nutrient elements used by plants, therefore they can be applied for purposes related to crop cultivation. The speed of producing vermicompost from waste depends on the nature of waste materials, and their fraction in addition to the earthworm species and concentration [33].

Conclusion

1. The study has shown that addition of saponin extract to waste participating in the vermicomposting process did not impact the size and mass of earthworm (*E. fetida*) populations, yet it negatively modified mature specimens in terms of their mass. Their reproduction was not affected for the duration of the experiment.
2. Addition of saponin extract to the mixture of waste used for vermicomposting process did not impact the contents of nitrogen, phosphorus, potassium, iron, and manganese, but it promoted reduced contents of sodium, calcium, copper and zinc in the fertilizers obtained.

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WPŁYW EKSTRAKTU SAPONINOWEGO NA WERMIKOMPOSTOWANIE WYBRANYCH ODPADÓW ORGANICZNYCH

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Abstrakt: Wermikompostowanie odchodów zwierzęcych i organicznych odpadów kuchennych stanowi jeden ze sposobów ich utylizacji. Celem badań było określenie wpływu ekstraktu saponinowego na cechy dżdżownic *E. fetida* użytych do wermikompostowania obornika od trzody chlewnej z dodatkiem organicznych odpadów kuchennych i celulozy oraz na skład chemiczny wyprodukowanych wermikompostów. W okresie prowadzonych badań, ekstrakt z *Quillaja saponaria* dodany do odpadów nie wpłynął na liczebność, masę populacji i rozmnażanie dżdżownic, ale modyfikował niekorzystnie masę osobników dojrzałych. Skład uzyskanych wermikompostów był zróżnicowany. Istotne różnice wykazano w zawartości sodu, wapnia, miedzi i cynku.

Słowa kluczowe: obornik od trzody chlewnej, organiczne odpady kuchenne, celuloza, *Eisenia fetida* (Sav.), saponiny, wermikompost

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NITROGEN AND SULPHUR FERTILIZATION ON YIELDING AND ZINC CONTENT IN SEEDS OF WINTER RAPE 'BALDUR' CULTIVAR

WPŁYW NAWOŻENIA AZOTEM I SIARKĄ NA PLONOWANIE I ZAWARTOŚĆ CYNKU W NASIONACH RZEPAKU OZIMEGO ODMIANY 'BALDUR'

Abstract: The research was conducted in order to determine the yield of winter rape seeds and zinc content in seeds as a result of fertilization with different doses of nitrogen and sulphur. A three-year field experiment was conducted according to the following scheme (9 treatments): 1. control – without fertilization; 2–4. nitrogen fertilization with doses of 134, 180, and 225 kgN $\cdot$ ha^{-1} in the form of ammonium nitrate (34 % N); 5–7. nitrogen fertilization with doses of 134, 180, and 225 kgN $\cdot$ ha^{-1} in the form of Saletrosan 26 Makro (26 % N and 13 % S); 8. sulphur fertilization with a dose of 60 kgS $\cdot$ ha^{-1} in the form of Saletrosan 26 Makro along with nitrogen complementation with ammonium nitrate to a dose of 180 kgN $\cdot$ ha^{-1}; 9. sulphur fertilization with a dose of 60 kgS $\cdot$ ha^{-1} in the form of Saletrosan 26 Makro along with nitrogen complementation with ammonium nitrate to a dose of 225 kgN $\cdot$ ha^{-1}. Sulphur application led to an increase in the yield of rape seeds and seed zinc content (and, as a result, also in the element uptake with yield), in comparison with the yield and zinc content in seeds collected from treatments without sulphur application.

Keywords: zinc, nitrogen fertilization, sulphur fertilization

Introduction

Optimal growth and development of cultivated plants requires access to indispensable macronutrients and microelements. Winter rape has high nutrient requirements, mainly for nitrogen and sulphur [1, 2]. It is cultivated, above all, as raw material for oil

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production, and the obtained waste products (extracted meal, oil cake, pomace) are used in animal feeding. In connection with the introduction of cultivars of double improved rape to cultivation as well as the introduction of changes in the technological process of acquisition of oil, it is intended to monitor changes in the level of mineral components in seeds of this plant. Zinc, which is a component of many enzymes and which is responsible for forming chelate bonds between enzyme and substrate, is one of microelements indispensable for proper development of plants [3, 4]. What is more, zinc participates in transformations of carbohydrates, proteins and phosphates [4]. Optimum zinc content in rape seeds is important when using them as a seed material, because this element is extremely important for proper plant growth in the first developmental stages [5, 6].

The aim of the research was to evaluate what effect nitrogen and sulphur, used in various doses, have on the yield and zinc content in winter rape, 'Baldur' cultivar, seeds.

Material and methods

The field experiment was conducted in the years 2009–2012 at the Experimental Station of the Department of Agrotechnology and Agricultural Ecology of the University of Agriculture in Krakow-Mydlniki. Brown earth soil, type – Luvisol, subtype – Stagnic Luvisol, textural group – silt, genus – formed from loess, is ranked among good wheat complex. Each year, spring barley was the forecrop for the double improved hybrid (Baldur) cultivar of rape.

Pre-sowing phosphorus fertilization in the form of superphosphate (40 % P_2O_5) amounted to 100 kg$P_2O_5 \cdot ha^{-1}$, and potassium fertilization in the form of potassium salt (60 % K_2O) amounted to 198 kg$K_2O \cdot ha^{-1}$. Doses of nitrogenous fertilizers, including the ones containing sulphur, were used according to the experiment scheme that included the following treatments: 1. control – without fertilization; 2–4. nitrogen fertilization in doses 134, 180, and 225 kgN $\cdot$ ha^{-1} in the form of ammonium nitrate (34 % N); 5–7 nitrogen fertilization in doses 134, 180, and 225 kgN $\cdot$ ha^{-1} in the form of Saletrosan 26 Makro (26 % N and 13 % S; this fertilizer is a mixture of ammonium nitrate and ammonium sulphate); 8. sulphur fertilization in a dose of 60 kgS $\cdot$ ha^{-1} in the form of Saletrosan 26 Makro complemented with nitrogen (ammonium nitrate) to a dose of 180 kgN $\cdot$ ha^{-1}; 9. sulphur fertilization in a dose of 60 kgS $\cdot$ ha^{-1} in the form of Saletrosan 26 Makro complemented with nitrogen (ammonium nitrate) to a dose of 225 kgN $\cdot$ ha^{-1}. Nitrogen in doses 134 kgN $\cdot$ ha^{-1} and 180 kgN $\cdot$ ha^{-1} was used three times, and in a dose of 225 kgN $\cdot$ ha^{-1} it was used four times. Each year in autumn, a starting dose of 30 kgN $\cdot$ ha^{-1} was applied to all the fertilization treatments, except the control (without fertilization).

The experiment was set up using the method of random blocks in 4 replications, and the area of each plot was 28 m^2 (15 m^2 for harvest).

Total precipitation in the period from sowing to inhibition of vegetation (VIII–XI) was between 119 mm in the season 2011/2012 and 281 mm in the season 2010/2011 (Table 1), and it was higher than the optimal total precipitation for rape in this period [7].

During the period of winter rest (XII–III), total precipitation was less diversified and it was between 93 mm in the season 2010/2011 and 143 mm in the season 2009/2010.

Table 1

Total precipitation in research years compared to multi-annual period 1977–2008 [mm]

Year	Month											
	VIII	IX	X	XI	XII	I	II	III	IV	V	VI	VII
Season 2009/2010	53.3	61.5	42.7	27.6	36.2	44.2	31.5	31.0	39.9	299.0	135.1	105.2
Season 2010/2011	127.5	112.8	14.0	26.6	43.4	25.9	8.1	15.2	77.7	48.0	33.0	186.4
Season 2011/2012	73.1	14.4	31.5	0.3	38.1	51.6	27.9	17.3	49.0	17.5	143.8	70.6
Multi-annual period 1977–2008	61.9	87.9	49.2	32.6	41.1	27.6	19.0	53.5	42.7	46.4	53.0	108.0
Optimum amount of precipitation acc. to Klatt									50	70	75	30

Particularly in the season 2010/2011 precipitation was lower than optimal precipitation in the period when rape rests [7]. From the beginning of vegetation to harvest, total precipitation exceeded the water requirements and was between 281 mm (season 2011/2012) and 579 mm (season 2009/2010). Cumulative water requirements during winter rape vegetation are approximately 400–525 mm [7]. Sums of precipitation, particularly in seasons 2009/2010 and 2010/2011, were higher. When comparing the data for the period of conducting the research with the data for the multi-annual period 1977–2008, it was established that the greatest differences occurred in May, June and August 2010, as well as in June 2012 (sums of precipitation were higher than the ones determined for the multi-annual period), and also in October 2010, March, September and November 2011, as well as in March 2012 (sums of precipitation were considerably lower).

During time of conducting the experiment, air temperature was generally lower than the mean temperature from the multi-annual period 1977–2008 (temperature higher than mean was found in August and April in all years of the research as well as in November 2009, July 2010, June 2011, and also in May and July 2012) (Table 2).

Table 2

Mean air temperature in research years compared to multi-annual period 1977–2008 [°C]

Year	Month											
	VIII	IX	X	XI	XII	I	II	III	IV	V	VI	VII
Season 2009/2010	18.6	12.9	9.8	5.7	–1.2	–6.3	–2.2	3.3	9.0	12.8	17.5	20.7
Season 2010/2011	18.4	12.3	8.7	3.1	–2.3	–1.2	–2.6	3.6	10.3	13.5	18.2	17.7
Season 2011/2012	19.0	14.1	8.6	2.1	1.6	–1.2	–6.6	4.4	9.4	15.0	17.4	20.3
Multi-annual period 1977–2008	18.2	13.1	10.0	3.9	0.2	–0.2	1.1	3.9	8.3	13.9	17.6	18.8

A temperature of over 20 °C [8] is the best for plant germination, and a temperature of 15–16 °C, which should drop gradually to 0 °C, is sufficient for growth and development before the winter rest. After recommencement of vegetation, air temperature should not be lower than 7–10 °C; 14.2 °C is optimal for the flowering stage, and 16.8 °C for seed filling.

During rape vegetation, plant protection measures were taken in accordance with agrotechnical recommendations. 10 days before rape harvesting, the plantation was dessicated with Reglone 200 SL in a dose of 2 $dm^3 \cdot ha^{-1}$.

Rape harvesting was carried out using a plot combine. Results regarding the seed yield were elaborated statistically, conducting an analysis of variance, and significance of the differences between treatments was verified by the Tukey's test at a significance level of $\alpha = 0.05$, using Statistica 10 software (StatSoft, Inc.).

Zinc content in rape seeds was determined in two replications, in average samples from each treatment, adding a sample of reference material to the series of analyses. The determination was carried out with inductively coupled plasma atomic emission spectrometry (ICP-AES) on JY 238 Ultrace apparatus. Preparing the samples for determination consisted in dry mineralization of the material (8 hours, 450 °C), evaporation with hydrochloric acid, and dilution of the remains in nitric acid solution [9].

Results and discussion

Dry matter yield from winter rape seeds in the research years is presented in Table 3. The data suggest that the highest yields of winter rape seeds in all the experimental treatments were obtained in 2012 (between 2.63 and 3.53 t of d.m. $\cdot$ ha^{-1}). However, they were lower than yields which can be obtained in optimal conditions according to many authors [10, 11].

Table 3

Rape seed yield [t of d.m. $\cdot$ ha^{-1}]

Treatment no.	Fertilization	2010	2011	2012	Mean
1	Control – without fertilization	1.74a*	1.85a	2.63a	2.07a
2	134 kgN $\cdot$ ha^{-1} ammonium nitrate	2.14b	2.38b	3.22bc	2.58b
3	180 kgN $\cdot$ ha^{-1} ammonium nitrate	2.31b	2.63c	3.14b	2.69bc
4	225 kgN $\cdot$ ha^{-1} ammonium nitrate	2.39b	2.86c	3.53c	2.93d
5	134 kgN $\cdot$ ha^{-1} Saletrosan 26 Makro	2.44c	3.20d	3.24bc	2.96d
6	180 kgN $\cdot$ ha^{-1} Saletrosan 26 Makro	2.52d	2.68c	3.25bc	2.82cd
7	225 kgN $\cdot$ ha^{-1} Saletrosan 26 Makro	2.50cd	3.32d	3.49c	3.10d
8	60 kgS $\cdot$ ha^{-1} Saletrosan 26 Makro + up to 180 kgN $\cdot$ ha^{-1} ammonium nitrate	2.50cd	2.79c	3.36bc	2.88d
9	60 kgS $\cdot$ ha^{-1} Saletrosan 26 Makro + up to 225 kgN $\cdot$ ha^{-1} ammonium nitrate	2.51d	2.51bc	3.33bc	2.78c

* Mean values in columns marked with the same letters do not differ statistically significantly at $\alpha = 0.05$, according to the Tukey's test.

Lower yields are caused mainly by the course of weather conditions during winter rape vegetation. It can be inferred from the amount and distribution of precipitation (Table 1) as well as the height of temperature (Table 2) during vegetation, which were most favorable for development of this species in the season 2011/2012 in comparison to the season 2009/2010 that was the least suitable.

In all years of the research, the lowest, significantly proven yields of rape seeds were found in the treatment without fertilization. On the other hand, fertilization of winter rape with various doses of nitrogen without sulphur in 2010 did not cause significant diversification of dry matter yield of seeds, whereas in the years 2011–2012 a tendency to a higher yield in the treatments with a higher nitrogen dose was found. In comparison with the yield from treatments fertilized with nitrogen without sulphur, introduction of this element along with Saletrosan 26 Makro resulted in an increase in mass of rape seeds, particularly in the years 2010 and 2011. Based on the amount of dry matter yield of rape seeds it was established that in order to satisfy plant demand for nitrogen it is better to use Saletrosan 26 Makro than ammonium nitrate.

There is no uniform position in the available literature regarding the effect of nitrogen and sulphur doses on the amount of rape seed yield. Wielebski and Wojtowicz [12] did not show that increase in sulphur doses had an effect on rape seed yield, whereas Sattar et al [13] established that the amount of yield increased along with the increase in nitrogen and sulphur doses. Wielebski [14] determined that rape seed yield increases under the influence of sulphur fertilization only in the case of a low content of the element in soil, whereas in conditions where plants have optimum supply of this element there is no effect of yield increase. On the basis of the own research it can be stated that nitrogen together with sulphur had a beneficial effect on the mean yield of dry matter from rape seeds from 3 years of the research, although differences among the treatments were not always statistically significant (Table 3). The seed yield from plants fertilized with Saletrosan 26 Makro in the smallest dose (134 kgN $\cdot$ ha^{-1} and 67 kgS $\cdot$ ha^{-1}) was by 15 % higher than the seed yield from plants fertilized only with ammonium nitrate in which the same dose of nitrogen was introduced. At the same time, this yield, at a dose of 225 kgN $\cdot$ ha^{-1} in the form of ammonium nitrate was in the same homogenous group as in the case of fertilization with 134 and 225 N $\cdot$ ha^{-1} applied in the form of Saletrosan 26 Makro, as well as with 60 kgS in the form of Saletrosan 26 Makro + 180 kgN in the form of ammonium nitrate.

Depending on the fertilization treatment, weighted mean of zinc content was within a range from 37.4 to 42.9 mgZn $\cdot$ kg^{-1} of d.m. (Table 4). These values are in accordance with the ones given by Banaszkiewicz [15] and Filipek and Harasim [16].

The zinc content in rape seeds in no treatment exceed the permissible value for rape intended for consumption or fodder, which is, respectively 50 mgZn and 100 mgZn $\cdot$ kg^{-1} of d.m. [17]. In own research, the highest zinc contents were found in rape seeds from treatments in which nitrogen and sulphur fertilization was used in doses 180 and 225 kgN $\cdot$ ha^{-1}, as well as 90 and 112.5 kgS $\cdot$ ha^{-1}. Such dependence occurred particularly in 2010 and 2011 (moreover, in 2011, sulphur fertilization in a dose of 60 kgS $\cdot$ ha^{-1} and nitrogen fertilization in a dose of 180 and 225 kgN $\cdot$ ha^{-1} had similar effect), and also in the case of mean values from 3 years.

Table 4

Zinc content in dry matter of rape seeds [mgZn · kg^{-1} of d.m.]

Treatment no.	Fertilization	2010	2011	2012	Weighted mean
1	Control – without fertilization	49.9	24.8	38.9	37.78
2	134 kgN · ha^{-1} ammonium nitrate	48.5	28.0	37.0	37.41
3	180 kgN · ha^{-1} ammonium nitrate	53.4	30.4	38.9	40.28
4	225 kgN · ha^{-1} ammonium nitrate	53.2	31.5	37.3	39.74
5	134 kgN · ha^{-1} Saletrosan 26 Makro	50.9	30.0	38.6	38.88
6	180 kgN · ha^{-1} Saletrosan 26 Makro	56.9	34.2	36.2	41.74
7	225 kgN · ha^{-1} Saletrosan 26 Makro	58.0	35.5	39.2	42.93
8	60 kgS · ha^{-1} Saletrosan 26 Makro + up to 180 kgN · ha^{-1} ammonium nitrate	51.9	34.1	37.3	40.49
9	60 kgS · ha^{-1} Saletrosan 26 Makro + up to 225 kgN · ha^{-1} ammonium nitrate	51.8	35.7	38.0	41.46

Similarly to own research, Kozlowska-Strawska [18] showed that rape plants fertilized with sulphur, particularly in sulphatic form, had the highest zinc content. In own research, sulphur was introduced to soil along with the Saletrosan 26 Makro fertilizer in the form of ammonium sulphate. In this context, the significance of soil reaction in the uptake of zinc by rape cannot be excluded.

Zinc amount uptaken along with dry matter yield from rape seeds is presented in Fig. 1. Since this amount is a product of seed yield mass and zinc content in it, the

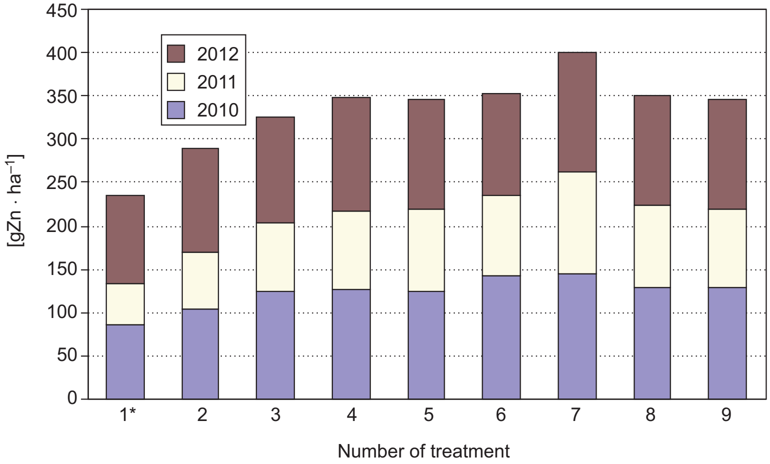

Fig. 1. Zinc amount [g Zn · ha^{-1}] uptaken along with dry matter yield from rape seeds: * 1. Control – without fertilization; 2–4. 134, 180 and 225 kgN · ha^{-1} in the form of ammonium nitrate, respectively; 5–7. 134, 180 and 225 kgN · ha^{-1} in the form of Saletrosan 26 Makro, respectively; 8. 60 kgS · ha^{-1} in the form of Saletrosan 26 Makro complemented with nitrogen (ammonium nitrate) to a dose of 180 kgN · ha^{-1}; 9. 60 kgS · ha^{-1} in the form of Saletrosan 26 Makro complemented with nitrogen (ammonium nitrate) to a dose of 225 kgN · ha^{-1}

differences among the research years are in accordance with the diversity in yielding and in the content of the component in yield. In the period of the experiment, rape from the non-fertilized soil took up the least zinc. At the same time, uptake of zinc with seed yield from plants fertilized with nitrogen with an addition of sulphur was higher than from plants fertilized only with nitrogen.

Rape is a plant that is relatively tolerant to zinc deficiency, but for proper growth and development this element is indispensable. Physiological role of zinc is connected with its function as an enzyme activator, particularly the ones participating in carbohydrate transformations and in synthesis of proteins. What is more, zinc guarantees a high level of protein in rape seeds [19], which is particularly important when the plants are intended for consumption or fodder.

Conclusions

1. The yields of rape seeds varied between the research years due to differences in weather conditions.
2. Application of sulphur in the fertilization contributed to an increase in the rape seed yields in comparison to yields from treatments without sulphur participation.
3. As a rule, the highest sulphur contents were determined in rape seeds from treatments where nitrogen and sulphur fertilization was used.
4. Uptake of zinc with seed yield from plants fertilized with nitrogen with an addition of sulphur was higher than from plants fertilized only with nitrogen.

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WPŁYW NAWOŻENIA AZOTEM I SIARKĄ NA PLONOWANIE I ZAWARTOŚĆ CYNKU W NASIONACH RZEPAKU OZIMEGO ODMIANY ‘BALDUR’

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Abstrakt: Badania wykonano w celu określenia wielkości plonu nasion rzepaku ozimego oraz zawartości w nich cynku w efekcie nawożenia zróżnicowanymi dawkami azotu i siarki. Doświadczenie polowe prowadzone w latach 2009–2012 obejmowało 9 obiektów: 1. kontrola – bez nawożenia; 2–4. nawożenie azotem w dawkach 134, 180 i 225 kgN $\cdot$ ha^{-1} w postaci saletry amonowej (34 % N); 5–7. nawożenie azotem w dawkach 134, 180 i 225 kgN $\cdot$ ha^{-1} w postaci Saletrosanu 26 Makro (26 % N i 13 % S); 8. nawożenie siarką w dawce 60 kgS $\cdot$ ha^{-1} w postaci Saletrosanu 26 Makro uzupełnione azotem (saletra amonowa) do dawki 180 kgN $\cdot$ ha^{-1}; 9. nawożenie siarką w dawce 60 kgS $\cdot$ ha^{-1} w postaci Saletrosanu 26 Makro uzupełnione azotem (saletra amonowa) do dawki 225 kgN $\cdot$ ha^{-1}. Wykazano, że zastosowanie siarki prowadziło do zwiększenia masy nasion rzepaku i zawartości w nich cynku (a w rezultacie także pobrania tego składnika z plonem), w porównaniu z plonem i zawartością cynku w nasionach zebranych z obiektów bez siarki.

Słowa kluczowe: cynk, nawożenie azotem, nawożenie siarką

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LITHIUM CONTENT IN SELECTED ROOT VEGETABLES AGAINST ITS CONTENT IN SOIL

ZAWARTOŚĆ LITU W WYBRANYCH WARZYWACH KORZENIOWYCH NA TLE JEGO ZAWARTOŚCI W GLEBIE

Abstract: In the first half of September 2003, 44 samples of cultivated root vegetables *ie* carrot, parsley, celery and beetroot at their consumption maturity, were collected from arable lands in the Miechowski county. Samples were gathered from the fields of considerable area (0.5–2.0 ha) vegetable cultivation. The collected plant material was subjected to dry mineralization, ash was dissolved in HNO_3 and obtained mineralizat was analysed. Soil samples were taken from the same locations as vegetables, from the depth of 0–25 cm. Basic physicochemical properties of the soil samples were determined by means of methods universally applied in agricultural chemistry. Total lithium content in the soils was determined after mineralization at a temperature of 450 ^oC, then digestion with a mixture of acids ($HClO_4$ and HNO_3) and dissolving in HCl. Content of this element soluble forms was determined after extraction with 0.1 mol $\cdot$ dm^{-3} HCl solution.

The total lithium content in the examined soils varied widely (2.79 to 12.20 mg $\cdot$ kg^{-1}), with a geometric mean of 7.78 mg $\cdot$ kg^{-1}. The content of the soluble forms of lithium extracted with 0.1 mol $\cdot$ dm^{-3} HCl solution varied from 0.057 to 0.251 mg $\cdot$ kg^{-1}, with a geometric mean of 0.119 mgLi $\cdot$ kg^{-1}. It was fund significant correlation between total lithium content and share of floatable fraction and colloidal clay in studied soils, as well as between content of soluble lithium forms and share of colloidal clay in soil. The lithium content in the vegetables varied depending on species and part of the plant. A geometric mean of lithium content in roots varied from 0.206 mgLi $\cdot$ kg^{-1} (parsley) to 0.365 mgLi $\cdot$ kg^{-1} (beetroot). Tops of vegetables contained 3–5 times more lithium than their roots. It was stated, that physicochemical properties of studied soils not uniformly affected lithium content in vegetables, what demonstrated values of simple correlation coefficients. Lithium content in roots of all vegetables and tops of beetroot and parsley depended on soluble forms of lithium content in soil. Moreover, lithium content in carrot roots as well as parsley roots and tops was affected

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by total lithium content in the soil. However, soil reaction had no significant effect on lithium content in organs of studied root vegetables.

Keywords: root vegetables, soil, lithium content

Introduction

Among trace elements microelements present in the natural environment are crucial for the correct growth and development of plants, as well as for the proper functioning of human and animal organisms. Usefulness of some elements (*eg* lithium) has not been fully recognized.

Lithium salts are relatively readily soluble in the soil water, therefore this cation is absorbed by plants proportionately to its concentration in the substratum [1]. The content and uptake of nutrients, including lithium, are determined by the content and form of a given element in soil, soil pH value, soil moistness and organic matter content, but also by heavy metal contents, the temperature and insolation, the kind and amount of applied mineral fertilizers and pesticides, number and composition of microflora present in the soil, the species and variety of plants and finally by other factors [2–6].

Currently, there is a growing interest in possibilities including waste materials of biological origin to the balance of organic fertilization [7]. These materials may be used for fertilization of some plants on condition that they do not contain heavy metals, nor are burdened with sanitary pollutants [8, 9].

Bioavailability of trace elements more or less determines consumptive or fodder value of agricultural products. Lithium salts are widely used in various industries and by modern technologies, so they may cause local pollution with this element and therefore affect plant chemical composition.

The investigations aimed at determining lithium content in root vegetables cultivated for consumption against its content in soil.

Materials and methods

The subject of investigations was selected root vegetables and soils from under their cultivation. In the first half of September 2003, 44 samples of cultivated root vegetables *ie* carrot, parsley, celery and beetroot at their consumption maturity, were collected from arable lands in the Miechowski county. Samples were gathered from the fields of considerable area (0.5–2.0 ha) vegetable cultivation, situated at the distance of more than 50 m from the main traffic routes. The analysed plant sample was an average of 12 individual ones (*ca* 1 kg of fresh mass). The collected plant material, after removing earthy parts, was washed and divided into roots and tops. After drying the examined samples were crushed and dry-mineralized. The obtained ashes were dissolved in nitric acid diluted with water (1 : 2, *v*/*v* ratio) and obtained solution was analysed.

From the same places as vegetables, soil samples were collected from the depth of 0–25 cm of arable lands. Each soil sample was an average of individual samples (0.5–1.0 kg of soil). Basic physicochemical properties were determined in the soil material by means of methods universally applied in agricultural chemistry [10]. Analyses comprised: soil texture by aerometric Bouyoucose and Casagrande's method in Proszynski's modification, pH by potentiometer in soil suspension in H_2O and in 1 mol · dm^{-3} KCl solution, and organic carbon content by Tiurin's method.

Total lithium content in the collected soil samples was assessed after previous mineralization at 450 ^oC and subsequent digestion in mineral acids mixture ($HClO_4$ and HNO_3) and dissolving in HCl [11]. The content of soluble forms of lithium was assessed after extraction with 0.1 mol · dm^{-3} HCl solution.

Lithium content was assessed in obtained plant and soil mineralizats and soil extracts by means of ICP AES method on JY 238 Ultrace apparatus.

The obtained results referring to lithium content in soils, plants and physicochemical soil properties were used for statistical computations, *ie* arithmetic and geometric means, standard deviation (SD), relative standard deviation (RSD) and linear correlation coefficients (r).

Results and discussion

Soil properties

The places of vegetable and soil samples collection were described in the first part of the paper [12].

The examined soils differed in respect of their texture, pH value, organic carbon content and the lithium content. pH value, assessed in water suspension fluctuated from 5.14 to 7.64, whereas in 1 mol · dm^{-3} KCl solution from 4.13 to 7.23. On the five degree acidification scale (pH_{KCl}), collected soil samples were divided into two groups: 11 samples were acid and slightly acid soils ($pH_{KCl} < 6.6$), whereas 33 samples were neutral ones ($pH_{KCl} \geq 6.6$).

On the basis of texture, collected soil samples were classified to the following agronomic categories: 5 represented medium soils with floatable particles content from 21 to 35 %, 36 samples were heavy soils with floatable particles content from 35 to 50 % and 3 – very heavy soils with over 50 % of floatable particles.

Total lithium content in the tested soils ranged from 2.79 mg · kg^{-1} to 12.20 mgLi · kg^{-1}, its geometric mean amounts 7.78 mg · kg^{-1}, and RSD = 27 %. The content of lithium soluble forms extracted in 1 mol · dm^{-3} HCl solution ranged from 0.057 mgLi · kg^{-1} to 0.250 mgLi · kg^{-1}, with geometric mean amounting 0.119 mgLi · kg^{-1} and RSD = 62 %. The share of these soluble lithium forms in total lithium content fluctuated from 0.83 to 3.05 %.

Ammari et al [13] revealed that the content of water extracted (soluble) lithium in the topsoil (0–20 cm) ranged from 0.95 to 1.04 mgLi · kg^{-1}, whereas in 20–40 cm layer from 1.06 to 2.68 mgLi · kg^{-1} depending on the region situated along the Jordan River valley.

Total content of lithium and its soluble forms extracted with 1 mol · dm^{-3} HCl solution in the studied neutral soils ($pH_{KCl} \geq 6.6$) was higher than in the acid and slightly acid ones ($pH_{KCl} < 6.6$) (Table 1).

Table 1

Lithium content in soil [mg · kg^{-1} d.m.] depending on soil pH

Parameter	Total content	Content of soluble forms
pH in 1 molKCl · dm^{-3} ≤ 6.5		
Range	4.80–9.30	0.064–0.250
Arithmetic mean	7.42	0.132
Geometric mean	7.28	0.118
RSD [%]	20	52
pH in 1 molKCl · dm^{-3} ≥ 6.6		
Range	2.79–12.20	0.057–0.204
Arithmetic mean	8.52	0.140
Geometric mean	8.14	0.135
RSD [%]	27	26

Explanation for Tables 1, 2 and 4: RSD – relative standard deviation.

Total lithium content dependent on examined soils texture and was twice higher in heavy and very heavy soils (with floatable particles content > 35 %) in comparison with medium soils (with floatable particles content ≤ 35 %) (Table 2).

Table 2

Content of lithium in soils [mgLi · kg^{-1}] depending on the share of soil fractions with ∅ < 0.02 mm

Parameter	Total content	Content of soluble forms
Content of < 0.02 mm fraction ≤ 35 %		
Range	2.79–7.58	0.057–0.202
Arithmetic mean	4.98	0.127
Geometric mean	4.59	0.115
RSD [%]	45	46
Content of < 0.02 mm fraction > 35 %		
Range	4.55–12.21	0.084–0.251
Arithmetic mean	8.54	0.139
Geometric mean	8.32	0.132
RSD [%]	22	31

Kosla [14] stated that heavy loamy soils contained bigger lithium amounts than light ones. The same relationship was confirmed by the research of Rogoz and Tabak [15] who found 14.8 mgLi · kg^{-1} in heavy soils, and 8.86 mgLi · kg^{-1} in light ones.

Statistical analysis of obtained results revealed that the physicochemical properties of the soils in which the vegetables were cultivated affected lithium content to various extent, as evidenced by simple correlation coefficients (Table 3).

Table 3

Simple correlation coefficients (r) between of lithium content in soils and selected physical and chemical properties

Soil property	Beetroot n = 40	Carrot n = 44	Parsley n = 44	Celery n = 32
Total lithium content				
pH_{KCl}	ns	ns	ns	ns
Share of fraction				
∅ < 0.02 mm	0.5830**	0.6173***	0.6038***	0.6182***
∅ < 0.002 mm	0.4278*	0.4058*	0.4034*	0.3369*
Content of soluble lithium forms				
pH_{KCl}	ns	ns	ns	ns
Share of fraction				
∅ < 0.02 mm	0.2265	0.2036	0.1766	0.1715
∅ < 0.002 mm	0.3899**	0.2570	0.2916*	0.1610

Explanation: n = number of soil samples; ns – not significant; r significant at: *p = 0.05; **p = 0.01; ***p = 0.001.

The pH of the studied soils did not have any significant influence either on total or soluble lithium forms content. A positive relationship occurred between total lithium content in the investigated soils and both floatable particles and colloidal clay share. Rogoz in his previous experiments [16] revealed that lithium content obtained in individual fractions in results of sequential fractioning of metals in soils was quite diversified depending on granulometric composition.

A positive dependence was also pointed out between lithium content in soil in forms extracted with 1 mol · dm^{-3} HCl solution and colloidal clay content (Table 3).

Lithium content in vegetables

Among the most valuable and vitamin rich vegetables used by households and possessing culinary values are: beetroot (*Beta vulgaris* var. *esculenta*), carrot (*Daucus carota*), parsley (*Petroselium sativum*) and celery (*Apium graveolens*). Lithium contents in plants depend on: the species, phase of development, analysed plant part, as well as content and forms of lithium present in soil [1, 12].

Plants absorb lithium in ionic form through exchange, proportionately to its content in soil [2, 3]. Ammari et al [13] demonstrated that lithium content was diversified depending on the species, as well as region of investigations. Lithium contents in citrus tree leaves fluctuated from 5 to 20 mgLi · kg^{-1} d.m., whereas in pepper leaves from 3 to 27 mgLi · kg^{-1} d.m.

In the Authors' own research lithium concentrations in the cultivated root vegetables were quite diversified depending on the species and analysed plant part. The arithmetic mean lithium content in roots was the largest in case of beetroot and showed the most changeability (RSD = 102.5 %), while in roots of other vegetables was around 20 to

45 % lower and showed smaller variability (RSD = 58.4–78.9 %) (Table 4). Larger lithium contents were found in the vegetable tops than in the roots, which evidences that this cation is easy subjected to translocation from roots to tops. This cation mean content in beetroot tops was about 5-fold higher than in roots, was the largest among studied vegetables and was the most diversified (RSD = 112.7 %). Arithmetic mean lithium contents in above-ground parts of other vegetables were from 3 to 3.5 times lower than in beetroot tops. Carrot, parsley and celery tops contained on average around thrice bigger amount of lithium than their roots, but showed a bit smaller variability than in beetroot tops (RSD = 78.0–98.0 %) (Table 4).

Table 4

Statistical parameters of lithium content [mg · kg^{-1} d.m.] in vegetable roots and tops

Parameter	Roots	Tops
	Lithium content [mg · kg^{-1} d.m.]	
Beetroot – *Beta vulgaris* var. *esculenta*		
Range	0.09–2.06	0.22–17.86
Arithmetic mean	0.468	2.741
Geometric mean	0.365	1.801
Standard deviation	0.369	3.088
RSD [%]	78.9	112.7
Carrot – *Daucus carota*		
Range	0.06–0.52	0.16–2.16
Arithmetic mean	0.243	0.775
Geometric mean	0.209	0.641
Standard deviation	0.130	0.500
RSD [%]	62.0	78.0
Parsley – *Petroselium sativum*		
Range	0.08–0.86	0.17–2.72
Arithmetic mean	0.270	0.743
Geometric mean	0.206	0.581
Standard deviation	0.211	0.569
RSD [%]	102.5	98.0
Celery – *Apium graveolens*		
Range	0.11–0.89	0.18–4.11
Arithmetic mean	0.363	0.896
Geometric mean	0.306	0.693
Standard deviation	0.212	0.764
RSD [%]	58.4	85.2

Jurkowska et al [2] and Rogoz [17] revealed that this element transport from stalks to leaves and seeds is weaker in plants growing in soil with higher lithium content than in plants cultivated in soil with natural content of this element.

Malinowska and Kalembasa [18] revealed a diversified lithium content in test plants, *ie* Italian ryegrass, maize and sunflower, depending on fertilization and liming. These authors the highest lithium bioaccumulation stated in sunflower, next in Italian ryegrass and finally in maize. Bibak et al [19] demonstrated that lithium content in of fresh mass of cabbage was on the level of 1.49 μgLi · kg^{-1}, whereas in Brussels sprouts 0.41 μgLi · kg^{-1} of fresh mass.

Physical and chemical properties of the studied soils in different extent affected lithium content in plants, as evidenced by simple correlation coefficients (Table 5).

Table 5

Simple correlation coefficients (r) between lithium content in root vegetables and selected properties of soil

Property	Beetroot n = 40	Carrot n = 44	Parsley n = 44	Celery n = 32
Roots				
Soil pH in KCl	0.1780	0.034	–0.1277	0.0685
Total content of lithium	0.0185	0.414*	0.2996*	0.3019
Content of lithium soluble forms	0.4690**	0.508**	0.6401***	0.6250**
Tops				
Soil pH in KCl	0.2379	–0.075	–0.1427	0.0901
Total content of lithium	0.2416	0.268	0.346*	0.2547
Content of lithium soluble forms	0.3652*	0.234	0.5514**	0.3202

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

Simple correlation coefficients revealed that the reaction of studied soils did not have any significant influence on lithium content both in tops and roots of vegetables. On the other hand, it was established that total lithium content in soil affected its content in roots of carrot, as well as in roots and tops of parsley. Moreover, values of correlation coefficients evidenced that content of lithium soluble forms determined this cation level in roots of all studied vegetables and in tops of beetroot and parsley as well (Table 5).

Bach [20] demonstrated that lithium is the element crucial for proper physical functions in goats and rats, which maintained on low-lithium ratios were shown to exhibit higher mortalities as well as reproductive and behavioral abnormalities. For example rats became less aggressive [21].

Lithium at levels naturally present in the diet may exert a powerful effect on behavior [22]. Dawson informed about evidence of correlation between low lithium contents of tap water and urine with higher mental hospital admissions due to psychosis, neurosis, schizophrenia, personality disorders and homicides [22]. A study carried out in Texas showed significantly more incidences of suicide, homicide and rape in counties where people drink water contained little or no lithium than in those with higher lithium concentration [23]. The animals responded differently to lithium supplement in fodder. Anke et al [24] stated that 20 mgLi · kg^{-1} added to goat or turkey feed led to slight changes in its consumption and in body weight gains. Ruminants are more sensitive to lithium burden than monogastric animals.

As presented Gupta et al [25] there are evidences that lithium plays an important role during the early fetal development because the high lithium contents were found in the embryo during the early gestational period. Lithium depletion causes low lithium status has a negative impact on homeostasis of glucose and insulin sensitivity in diabetic patients and lithium supplementation may manage this disease [22]. Moreover, 72 % of diabetic patients had low lithium content in serum, and of control ones only 10 % of population.

So far there have been few data on lithium content in food products or its consumption by people available in the literature. For this reason investigation of lithium content in vegetables is very important and may be useful for elucidation this issue.

Długaszek et al [26] suggested allowable lithium contents in 6 groups of food products, *ie* cereals 4.405 mgLi $\cdot$ kg^{-1}, vegetables 2.327 mgLi $\cdot$ kg^{-1}, potatoes 1.305 mgLi $\cdot$ kg^{-1}, dairy products 0.5 mgLi $\cdot$ kg^{-1} and fish 3.15 mg Li $\cdot$ kg^{-1}. Schrauzer [27] determined considerable amounts of lithium in yeast *Saccharomyces cerevisiae*, *ie* 115–400 mgLi $\cdot$ kg^{-1}.

Daily requirement for lithium of an adult weighing 70 kg is 1000 μg, *ie* 14.4 μg $\cdot$ kg^{-1} of body weight. Długaszek et al [25] demonstrated also that the results obtained are approximate to results published by Belgian authors. Van Cauwenbergh et al [28] provided that average daily lithium consumption by a group of students participating in the investigations fluctuated from 3.9 in Brussels to 12.2 μg $\cdot$ d^{-1} in Antwerp and Vilwoorde. Lithium intake ranged from 1.2 to 15.2 μg $\cdot$ d^{-1}, and mean value for adult amounted 8.6 ± 4.6 μg $\cdot$ d^{-1} and was lower than in other countries. In the paper are also presented data concerned daily lithium consumption in various countries, *eg* Canada 21.6 μg, Germany 182–546 μg and Great Britain 107 μg $\cdot$ d^{-1}. According to Schrauzer [27] considerable quantities of this element are consumed by the citizens of China (1560 ± 1009 μg $\cdot$ d^{-1}).

Conclusions

1. Lithium content in vegetable roots depended on the species and analysed plant part. Mean geometric lithium content in beetroot was 0.365 mgLi $\cdot$ kg^{-1}, in the roots of carrot 0.209 mgLi $\cdot$ kg^{-1}, parsley 0.206 mgLi $\cdot$ kg^{-1} and celery 0.306 mgLi $\cdot$ kg^{-1}. Lithium content in the cultivated vegetables was determined by the content and form in which it occurred in soil.

2. Larger lithium contents were registered in the tops than in roots of the analysed vegetables, what indicates an easy translocation of this element from roots to above-ground parts.

3. It was demonstrated that physical and chemical properties of the studied soils to various extent influenced lithium content in vegetables as evidenced by values of simple correlation coefficients.

4. Determining lithium contents in food products and its consumption is crucially important because this element participates in many important life processes of humans and animals.

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ZAWARTOŚĆ LITU W WYBRANYCH WARZYWACH KORZENIOWYCH NA TLE JEGO ZAWARTOŚCI W GLEBIE

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Abstrakt: W pierwszej połowie września 2003 r. na terenie powiatu miechowskiego pobrano 44 próbki warzyw korzeniowych, tj. marchwi, pietruszki, selera oraz buraka czerwonego. Próbki pobierano z pól o znaczącym areale (0,5–2,0 ha) uprawy warzyw z przeznaczeniem na cele konsumpcyjne. Zebrane próbki warzyw poddano mineralizacji na sucho, popiół roztworzono w HNO_3, a uzyskane mineralizaty poddano analizie. Z tych samych miejsc, na których uprawiano warzywa korzeniowe, pobrano próbki glebowe z głębokości 0–25 cm. W próbach glebowych oznaczono podstawowe właściwości fizykochemiczne metodami standardowymi stosowanymi w chemii rolnej. Całkowitą zawartości litu w glebach oznaczono po ich wcześniejszej mineralizacji w temperaturze 450 ^{o}C, a następnie wytrawieniu w mieszaninie kwasów ($HClO_4$ i HNO_3) i roztworzeniu w HCl. Zawartość rozpuszczalnych form tego pierwiastka oznaczono po ich wyekstrahowaniu roztworem HCl (0,1 mol · dm^{-3}).

Całkowita zawartość litu w badanych glebach wahała się w szerokim zakresie (2,79–12,20 mgLi · kg^{-1}), a średnia geometryczna wynosiła 7,78 mgLi · kg^{-1}. Natomiast zawartość rozpuszczalnych form litu wyekstrahowanych HCl o stężeniu 0,1 mol · dm^{-3} wahała się od 0,057 do 0,251 mgLi · kg^{-1} (ze średnią geometryczną 0,119 mgLi · kg^{-1}). Stwierdzono istotną dodatnią korelacje pomiędzy całkowitą zawartością litu a zawartością części spławianych oraz iłu koloidalnego w badanych glebach, a także pomiędzy zawartością rozpuszczalnych form litu a zawartością iłu koloidalnego.

Zawartość litu w zebranych warzywach była zróżnicowania w zależności od gatunku i organu rośliny. Średnia geometryczna zawartość litu w korzeniach wynosiła od 0,206 mgLi · kg^{-1} (pietruszka) do 0,365 mgLi · kg^{-1} (burak czerwony). Części nadziemne warzyw zawierały 3–5 razy więcej litu niż korzenie. Wykazano, że właściwości fizykochemiczne badanych gleb w niejednakowym stopniu wpływały na zawartość litu w warzywach, czego dowodzą wartości współczynników korelacji prostej. O zawartość litu w korzeniach wszystkich badanych warzyw oraz naci buraka i pietruszki decydowała zawartość rozpuszczalnych form litu w glebie. Ponadto zawartość litu w korzeniach marchwi oraz korzeniach i naci pietruszki zależała od całkowitej zawartość tego pierwiastka w glebie. Natomiast odczyn gleb nie miał istotnego wpływu na zawartość litu w organach badanych warzyw korzeniowych.

Słowa kluczowe: warzywa korzeniowe, gleba, zawartość litu

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MOLD CONTAMINATION OF COMMERCIALLY AVAILABLE HERBAL PRODUCTS AND DIETARY SUPPLEMENTS OF PLANT ORIGIN

ZAGROŻENIE ZANIECZYSZCZENIA GRZYBAMI PLEŚNIOWYMI ZIÓŁ ORAZ SUPLEMENTÓW DIETY POCHODZENIA ROŚLINNEGO DOSTĘPNYCH NA RYNKU

Abstract: Recent years have witnessed a rapid development of the dietary supplement market and a revived interest in herbal products used for therapeutic purposes. Herbs and medicinal plants have been used in traditional medicine for centuries. The concentrations of active substances in industrially processed plant extracts are many times lower than those found in the original plant material. For this reason, long-term of use herbal preparations is safe, and it does not require medical consultation. Herbs and medicinal plants have a complex composition, and recent research indicates that they may produce adverse reactions with food ingredients or pharmaceuticals. Molds, mainly fungi of the genera *Fusarium*, *Penicillium* and *Aspergillus* which colonize growing plants, are thermophilous organisms that can survive drying and heat processing, and they can find their way to the final product. Those fungi produce mycotoxins, metabolites which are toxic for humans.

In our study, fungi of the genera *Aspergillus* and *Fusarium* were determined in commercially available fresh herbs, herbal teas and herbal dietary supplements in the form of tablets.

Keywords: molds, herbs, dietary supplements, *Aspergillus*, *Fusarium*

Introduction

Herbs constitute a large group of plants containing active substances which may deliver health benefits for consumers. In addition to herbs, this category of plants also includes trees and shrubs which have been used as spices and medicinal products since antiquity. The therapeutic properties of herbs are determined by their chemical composition, mainly the presence of alkaloids, anthra-compounds, azulenes, phenols, flavonoids, tannins, cardiac glycosides, glucosinolates, pectins, saponins and mucila-

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ginous compounds [1, 2]. Despite the predominance of chemical medications on the contemporary market, there has been a revived interest in medicinal plants which are easily available and pose an alternative to synthetic drugs. There are two categories of medicinal herbs:

– herbal medicines – herb plants (mint leaves, lemon balm leaves, dandelion root) and herbal mixes;

– herbal formulations – herbs in the form of tablets, dragées, capsules and liquids (dry extracts, condensed extracts, infusions, essential oils) [3].

Fresh and dried herbs are also used to bring out and enhance the natural flavor and aroma of food [4]. Owing to their medicinal properties, herbs ease digestion, increase nutrient availability and boost natural immunity. Herbs fortify hair, nails and skin, and they are widely used in the cosmetics industry.

Poland has been a significant supplier and exporter of herbs for decades. Campaigns promoting natural foods and cosmetics have turned the consumers' attention to products containing herbs and spices [5]. Herbal raw materials are subject to strict control which contributes to the quality of the final product and promotes the development of new formulations. Herbs are used as fresh and dried plants (whole or ground plant fragments, mixes containing several plants), essential oils, extracts and microcapsules [6]. Dried herbs are highly popular due to their long shelf-life. Dried herbs and spices can, however, be colonized by fungi which produce harmful mycotoxins [7].

Raw herbs can act as hosts for microorganisms which colonize plants, soil, water and air. Plant communities are popularly colonized by molds of the genera *Alternaria*, *Fusarium*, *Cladosporium*, *Penicillium* and, less frequently, *Aspergillus*, *Trichoderma*, *Mucor* and *Rhizopus*. The size of fungal populations in fresh plant matter may exceed 10^6 CFU/g. Microbiological soil pollutants may also be introduced during the harvesting, transport and storage of plants when the number and abundance of mold communities, in particular of the genera *Penicillium*, *Fusarium*, *Alternaria*, *Cladosporium* and *Verticillium,* grows rapidly [8, 9]. Molds representing the genera *Alternaria*, *Aspergillus*, *Cladosporium* and *Penicillium* are transferred from the air to herbal raw materials [10, 11]. The composition of the microflora from this source is determined mainly by the degree of urban development in the herb growing area, and it increases considerably in the vicinity of cities.

Dried herbs may undergo microbiological contamination at nearly every stage of production, beginning from harvesting and drying to packaging which should protect the final product from adverse environmental impacts [5, 11, 12]. Molds colonizing raw herbs produce mycotoxins, secondary metabolites which pose a health hazard for humans and animals. Those low-molecular weight compounds are weakly polar, and they are not damaged by pasteurization or high temperature. They are degraded in an alkaline environment and under exposure to UV radiation [13]. The most prevalent mycotoxins include aflatoxins, ochratoxin A, patulin, trichothecenes, sterigmatocystin and vomitoxin. Subject to fungal species and their habitat conditions, the produced mycotoxins may deliver mutagenic, teratogenic, neurotoxic and nephrotoxic effects [14–16]. Herbal plants are most often colonized by the following mold genera and species: *Alternaria* sp*.*, *Aspergillus* sp. (*A. amstelodami*, *A. sydowii*), *Chaetomium* sp., *Cladosporium* sp., *Fusarium* sp., *Mucor* sp., *Penicillium* sp., *Rhizopus* sp., *Trichoderma* sp. and *Verticillium* sp. The size of fungal populations is estimated at 10^1–10^6 CFU/g [5, 8, 17].

Herbal ingredients are found in foods, spice mixes and dietary supplements, and their microbiological purity is a highly important criterion while evaluating their processing suitability. Herbs, in particularly dried plants, are often carriers of microorganisms which are introduced into the final product. Evaluations of the medicinal properties and sensory attributes of herbs should, therefore, be accompanied by microbial and fungal analyses.

The objective of this study was to evaluate the degree of mold contamination in commercially available fresh herbs, herbal teas and herbal dietary supplements in the form of tablets.

Materials and methods

The experimental material comprised fresh basil, lemon balm and mint, as well as dried herbs, herbal teas and dietary supplements. Herbs were harvested from an organic farm, a farm where plants were sprayed with Topsin M 500SC fungicide, and pots:

– Basil I – pot, Santa Maria (Swedoponic, Polska),
– Basil II – pot, “Pokarm życia” horticultural-breeding farm, Poland,
– Basil III – treated with fungicide,
– Basil IV – organic farm,
– Lemon balm I – pot, Santa Maria (Swedoponic, Polska),
– Lemon balm II – pot, “Pokarm życia” horticultural-breeding farm, Poland,
– Lemon balm III – treated with fungicide,
– Lemon balm IV – organic farm,
– Mint I – pot, “Pokarm życia” horticultural-breeding farm, Poland,
– Mint II – organic farm.

Dried herbs and herbal teas were purchased in grocery stores and the Tesco supermarket, and dietary supplements (herbal tablets) were acquired from pharmacies in the city of Lublin.

Mycological evaluation

Fresh herbs: Mycological analyses were performed on 7–8 leaves from mature shoots without flower buds. The leaves were washed, dried and chopped. Two samples of 5 g each were placed on Petri dishes lined with moistened filter paper and incubated at 23 $^{\circ}$C. After 7 days, fungal cultures were transferred to potato dextrose agar (PDA) with the addition of chloramphenicol (100 mg/dm^3) and incubated at 28 $^{\circ}$C for 5 days.

Dried herbs and herbal teas: Three samples of 5 g each were placed on Petri dishes lined with moistened filter paper. The procedure was identical to that applied to fresh herbs.

Herbal tablets: Five tablets were randomly selected from the package. They were ground in a ceramic mortar, and three samples of 5 g each were incubated on moistened filter paper at 23 °C. After 7 days, fungal cultures were transferred to a PDA medium.

Fungal strains were identified based on mycological keys [18, 19].

Results

Molds are common in the environment, they are characterized by low sensitivity to external factors and the ease of propagation. Molds develop at a temperature of 18 to 32 °C, and they can survive in a wide temperature range of 6 to 60 °C (in particular in aerobic habitats, but also under anaerobic conditions) and at pH of 2–8.5 [20]. Molds remain stable in environments with relative humidity of 20 to 75 %, and they are thermophilous and thermotolerant organisms [21]. Food contamination with molds, their spores and toxic metabolites is difficult to control, and it poses a significant health risk for consumers.

Herbal teas and tables have a very low moisture content in the range of 7–12 %, therefore, they do not offer a supporting habitat for microbial growth. Most molds produce spores which can survive in highly unsupportive environments. Spores are resistant to drying temperatures (the optimal temperature for drying herbal products is 35–50 °C) and low humidity levels. They remain dormant under the above conditions, but when the moisture content of plant material increases to 30 % due to inadequate storage, spores begin to germinate and grow. Molds can develop in much drier habitats than bacteria, therefore dried plants and herbs are more likely to be colonized by molds than bacteria.

Most fungi isolated from herbs and herbal teas belong to the genera *Fusarium* and *Aspergillus*, pathogens which are commonly found in the environment. Those molds are generally harmless, but selected species produce toxic metabolites. Food products offer a highly supportive habitat for microbial growth, and molds colonizing food ingredients are often a source of secondary contamination. Molds observed in the examined material (Table 1) were members of 7 genera, and the presence of *Aspergillus* and *Fusarium* was observed in all studied herbs. Representatives of the genera *Alternaria* and *Penicillium*, followed by *Mucor*, *Rhizopus* and *Uclodium* sp. were less frequently noted. Molds of the genera *Cladosporium* and *Trichoderma* were not determined. Similar results were reported by Wojcik-Stopczynska et al [22, 23] in whose study, herbs were most frequently colonized by fungal genera of *Alternaria*, *Botrytis*, *Penicillium*, *Fusarium* and *Aspergillus*. Our results corroborate the findings of Halt and Klapec [24] who evaluated the contamination of herbal teas with microbial pathogens. In the cited study, a prevalence of the genera *Penicillium, Aspergillus, Cladosporium* and *Alternaria* was determined in experimental material, and none of the analyzed samples were free of molds.

Rizzo et al [25] found 56 strains of toxin-producing fungi in dried herbaceous plants grown in Argentina. More than half of the samples contained strains of the genus *Aspergillus*, and 16 % of the samples were contaminated by the genus *Fusarium*. The above authors observed that the number of toxin-producing fungi varied depending on

Table 1

Mold strains isolated from fresh herbs

Strain	Basil I	Basil II	Basil III	Basil IV	Lemon balm I	Lemon balm II	Lemon balm III	Lemon balm IV	Mint I	Mint II
Aspergillus fumigatus	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +		
Aspergillus niger	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Penicillium spp.	+ +	+ +	+ +	+ +						
Aspergillus flavus	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +		
Fusarium avanaceum	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Fusarium culmorum	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Fusarium oxysporum	+ +			+ +	+ +	+ +	+ +			
Fusarum solani		+ +		+ +	+ +	+ +				
Alternaria alternata	+ +	+ +	+ +	+ +			+ +		+ +	+ +
Mucor				+ +						
Rhizpus	+ +		+ +							
Uclodium sp.									+ +	+ +

the herb (*Melissa officinalis* L and *Mentha piperita* L) growing area, and none of the examined samples were free of contaminants. In our experiment, the predominant pathogens were *Aspergillus niger* and *Fusarium* strains, *F. avanaceum* and *F. culmorum* (Fig. 1).

The above species colonized all of the examined herbs, which is a serious cause for concern because they produce toxic metabolites. At higher concentrations, aflatoxins and *Fusarium* toxins, in particular zearalenone and deoxynivalenol, can lead to intestinal inflammations, genetic code damage and liver cell damage [26]. In the long-term, the studied pathogens exert teratogenic effects. *Aspergillus flavus* and *Aspergillus niger* were also prevalent molds (23.6 %) in a study by Bugno et al. [27] who examined herbs from various regions of Brazil. Similar results were reported by Mandeel [28] who isolated *A. flavus* from all evaluated mixes of more than 50 plants and herbs.

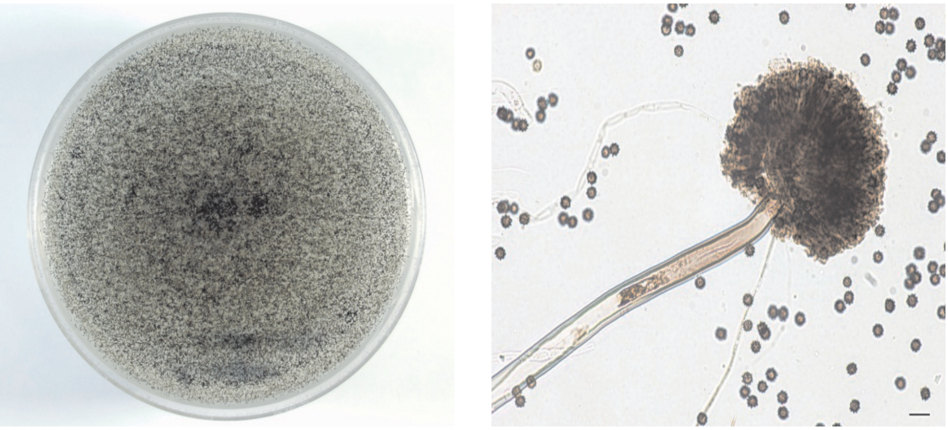

Fig. 1. *Aspergillus niger* isolated from basil, mint and lemon balm

In this experiment, the highest resistance against pathogens was observed in mint plants grown both in pots and in an organic farm. The above can be attribute to the presence of active substances in mint essential oil and various polyphenol compounds. Other authors have observed that mint extracts have bactericidal and fungicidal effects, and they inhibit the growth of fungi of the genera *Aspergillus*, *Penicillium* and *Fusarium* [29–31]. For this reason, fresh and dried mint as well as mint teas are least susceptible to colonization by toxin-producing fungi.

Basil is at the greatest risk of mold contamination. No significant differences in the number of pathogenic molds were observed between basil treatments. Basil grown in an organic farm was colonized by 10 mold strains, and plants from the remaining treatments – by 8 and 9 strains. The above indicates that the applied fungicides are ineffective and that molds have developed a resistance to active substances with fungicidal properties that have been in use for at least 10 years.

The bactericidal and fungicidal properties of active substances contained in basil essential oil have been studied in various research centers. Oxenham et al [32] demonstrated that basil essential oil inhibits the growth of *Botrytis fabae*. Koba et al [33] and Hussain et al [34] confirmed the bactericidal effects of basil oil on Gram-positive and Gram-negative bacteria, whereas basil extracts were relatively ineffective in combating fungi of the genus *Aspergillus* (MIC higher than 500 mg/dm^3). Kocic-Tanackov et al found that ethanol and methanol extracts of basil exhibited fungicidal activity against laboratory-grown and naturally occurring fungal pathogens, but in their study, only two strains of each species were analyzed [35].

The results of analyses of dried herbs and herbal teas are presented in Table 2.

Similarly to fresh herbs, the prevalent pathogens colonizing dried herbs and herbal teas were *Aspergillus niger, F. avanaceum* and *F. culmorum*. Sage was most susceptible to contamination, whereas mint was most resistant to molds regardless of the brand and type of packaging. Zimowska demonstrated that sage is highly susceptible to colonization by various species of pathogenic fungi, and the majority of isolated strains belonged to the genus *Fusarium*, *Rhizoctonia solani* and *Phoma exigua* [36].

Table 2

Mold strains isolated from dried herbs and herbal teas

Strain	Sage	Sage leaf	Mint	Mint	Mint leaf	Lemon balm	Lemon balm	Lemon balm leaf
Aspergillus fumigatus	+ + +	+ + –				+ – +	+ + +	– + +
Aspergillus niger	+ + +	+ – +	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +
Aspergillus flavus	+ + +	– + +				– – +	+ + +	
Penicillium spp.	+ – –	+ + –						
Fusarium avanaceum	+ + +	+ + +		+ + +	+ – –	+ + +	+ + +	+ + +
Fusarium culmorum	+ + +	+ – +	+ + –	+ + +	+ – –	+ – +	+ + +	+ + +
Fusarium oxysporum	+ – +	+ – +				+ + +	+ + +	+ + –
Fusarium solani	+ – –	+ – +				+ + +	+ + +	
Alternaria alternate	+ + +	+ + +	– – +	+ + +			+ – +	
Rhizopus		+ + +						

Lemon balm was relatively resistant to fungal strains, and pathogenic colonization levels were particularly low in lemon balm leaves. The above could be attributed to the high quality of raw material and optimal storage conditions at the supplier’s facility. The results of our study suggest that storage conditions (optimal temperature, stable humidity levels) and the quality of the production process largely affect contamination of the final product. Pokrzywa et al. analyzed mycotoxin contamination of foodstuffs, including dried herbs and spices. The presence of aflatoxins was determined due to contamination with fungi of the genus *Aspergillus* [16].

In view of the growing popularity of herbal remedies in Poland, dried herbal tablets have been introduced on the market for greater convenience. Tablets are easy to ingest, and they eliminate the brewing process. The risk that spores will develop into active molds in herbal tablets is reduced, but only if high quality raw materials are used. In our study, lemon balm, mint, sage and lovage tablets were analyzed (Table 3).

Table 3

Mold strains isolated from herbal tablets

Strain	Mint	Lemon balm	Sage	Lovage
Aspergillus fumigatus	+	+	+	+
Aspergillus niger	+	+	+	+
Penicillium spp.			+	+
Aspergillus flavus			+	+
Fusarium avanaceum		+	+	+
Fusarium culmorum		+	+	+
Fusarium oxysporum		+	+	+
Fusarium solani			+	+
Alternaria alternata			+	+

The results indicate that mint was most resistant to fungal colonization due to the bactericidal and fungicidal properties of its active substances. Only the most prevalent strains of the genus *Aspergillus* were found in mint. Sage and lovage were colonized by 9 strains of pathogenic fungi.

Our findings demonstrate that plant material not contaminated by molds and their toxic metabolites is very difficult to acquire. The microbiological purity of fresh and dried herbs, herbal and black teas has been investigated by numerous authors, and the presence of mold fungi was reported in all studies. Mycotoxin levels determined in various research centers indicate that safe toxin levels are exceeded in only a small percentage of foodstuffs. However, the presence of toxic metabolites in food and the environment poses a health risk for consumers.

The results of our study indicate that fungal contamination of herbal products is a common problem. This issue can be addressed by changing farming practices, using advanced fungicides that inhibit the growth of various pathogens and storing herbal products in environments characterized by a constant temperature and humidity.

Conclusions

1. The analyzed fresh and dried herbs as well as herbal tablets were contaminated with toxin-producing fungi.
2. The predominant pathogens were fungi of the genera *Aspergillus* and *Fusarium* which colonized the majority of the analyzed samples.
3. Mint was characterized by the highest resistance to mold contamination, which can be attributed to the bactericidal and fungicidal properties of the active substances found in mint essential oil.

4. Foodstuff contamination with molds which produce mycotoxins harmful for humans and animals poses a serious epidemiological risk.

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ZAGROŻENIE ZANIECZYSZCZENIA GRZYBAMI PLEŚNIOWYMI ZIÓŁ ORAZ SUPLEMENTÓW DIETY POCHODZENIA ROŚLINNEGO DOSTĘPNYCH NA RYNKU

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Abstrakt: W ostatnich latach nastąpił szybki rozwój rynku suplementów diety i powrót do preparatów ziołowych stosowanych w profilaktyce i w lecznictwie. Ma to swoje uzasadnienie tym, że zioła i rośliny lecznicze były od lat stosowane z powodzeniem w medycynie tradycyjnej. Używane w przemyśle farmaceutycznym wyciągi z roślin zawierają w swoim składzie stężenia substancji aktywnych wielokrotnie niższe od tych zawartych w samych roślinach. Gwarantuje to bezpieczeństwo długotrwałego stosowania bez konsultacji z lekarzem. Jednak zioła i inne rośliny o właściwościach leczniczych mają bardzo złożony skład i coraz częściej okazuje się, że mogą łatwo reagować w sposób niekorzystny ze składnikami żywności czy innymi farmaceutykami. Dodatkowo dużym zagrożeniem okazują się grzyby pleśniowe, głównie z rodzaju *Fusarium*, *Penicillium* i *Aspergillus*, które kolonizują rośliny w stanie naturalnego wzrostu, a w procesie suszenia i przetwarzania ze względu na swoją termofilność przechodzą do produktu gotowego. Są one szczególnie niebezpieczne, ponieważ mają zdolność wytwarzania toksycznych dla człowieka produktów przemiany materii, mikotoksyn.

Jak wynika z przeprowadzonych badań własnych, grzyby z rodzaju *Aspergillus* i *Fusarium* występują nie tylko na świeżych ziołach dostępnych w sprzedaży, ale również w herbatkach ziołowych oraz w ziołowych suplementach diety w postaci tabletek.

Słowa kluczowe: pleśnie, zioła, suplementy diety, *Aspergillus*, *Fusarium*

Varia

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18. 2009 CEC ECOpole ’09 Piechowice
19. 2010 CEC ECOpole ’10 Piechowice
20. 2011 CEC ECOpole ’11 Zakopane
21. 2012 CEC ECOpole ’12 Zakopane
22. 2013 CEC ECOpole ’13 Jarnołtówek

ZAPRASZAMY DO UDZIAŁU W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI ECOpole ’14 W DNIACH 15–18 X 2014 r.

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

Będzie to **dwudziesta trzecia z rzędu** konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotyczącym różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w Hotelu Ziemowit w Jarnołtówku.

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Prof. dr hab. inż. Maria Wacławek
Przewodnicząca Komitetu Organizacyjnego
Konferencji ECOpole '14

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