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VARIA

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Damian PANASIUK[1, 2], Anna GŁODEK[1]
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SCENARIOS OF MERCURY EMISSION TO AIR, WATER AND SOIL IN POLAND TO YEAR 2020

SCENARIUSZE EMISJI RTĘCI DO POWIETRZA, WÓD I GLEBY W POLSCE DO ROKU 2020

Abstract: Among European countries Poland has fourth place in mercury emission to atmosphere in 2005, mainly due to hard and brown coal combustion in energy sector. NILU Polska estimated Polish national mercury emission to air and loads discharged to water and soil for the base year 2008, then it prepared mercury emission scenarios to 2020. Inventory of emission to the atmosphere covered industrial processes, mercury use in products and dental practice. Loads of mercury discharged to water and soil were estimated for large and medium industrial facilities, municipal waste water treatment plants and also for potential mercury release from municipal landfills and dental amalgam in buried bodies. In comparative Status Quo scenario it was assumed that current practices and methods of mercury emission control will be maintained, but the growth of production and consumption will lead to the increase of mercury emission. In EXEC (*EXtended Emission Control*) scenario mercury emission to air will fall from 17.7 Mg in base year to 6.3 Mg in 2020 and total emission to air, water and soil from 25.7 to 8.9 Mg. In MFTR (*Maximum Feasible Technical Reduction*) scenario emission to air will achieve level 2.8 Mg Hg in 2020 and total emission to the environment – 3.6 Mg Hg annually.

Keywords: emission scenarios, mercury, air, water, soil

Problem of mercury emission to environment

Mercury is one of toxic heavy metals introduced to environment as a result of human activity. However considering its high volatility mercury is not only regional pollution as SO_2, NO_x, Cd or Pb. Mercury can appear in many chemical forms, that is crucial for

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further changes of mercury and its compounds. *Gaseous elemental mercury* (GEM or Hg^0) is one of mercury forms. Mercury can appear also in oxidized forms: *reactive gaseous mercury* (RGM or Hg^{2+}) and mercury adsorbed on dust – *total particulate mercury* (TPM). The sum of all gasous mercury compounds and elemental mercury is defined as *total gaseous mercury* (TGM).

Atmospheric lifetime for gasous elemental mercury to 18 months [1] places mercury in group of global pollutants. Main problem of mercury pollution is bioaccumulation and negative influence of methyl mercury compounds (methylmercury and dimethylmercury) on human populations eating many fishes and marine mammals. The most known case of methylmercury poisoning is ecological disaster which happened in Minamata Bay in Japan in the fifties. There were damages of nervous system of people eating fish and crab meat. Death of almost 1800 and diseases of further thousands people were officially recognised.

Human fetus is most vulnerable for methylmercury exposure. Mercury filtrates from mother's blood to fetus blood and causes neurological damages manifested in later period as lower intelligence quotient or even autism. Therefore, resolution of global mercury convention on mercury trade limitation and emission reduction is planned until 2013.

Mercury emission inventory for base year

Among European countries Poland had fourth place (second place among EU member states after Germany) in mercury emission to atmosphere in 2005 [2]. Hard and brown coal combustion in Polish energy sector is main source of this emission. Annually combusted 80 million Mg of hard coal (40 million Mg for electricity generation) and 60 million Mg of lignite contain above 20 Mg of mercury. Review of data on mercury content in Polish coals [3] shows that scopes of content are different. Values of 100 mg/Mg for hard coal and 250 mg/Mg for lignite are generally published as averages. The majority of research studies show higher mercury content in lignite than in hard coal. Amount of mercury emitted to air depends on the use of primary measures – coal washing – as well as on dedusting and desulfurization method efficiencies – mercury emission reduction in Poland achieves 70 %.

NILU Polska estimated Polish national mercury emission to air and loads discharged to water and soil for the base year 2008 [4]. Inventory of emission to the atmosphere covered industrial processes, mercury use in products and dental practice. Emission from industrial processes and fuel combustion in residential sector (15.75 Mg) was estimated as annual average, based on official emission inventories of IOS-KOBiZE for years 2005–2007.

Mercury emission to air from mercury use in products was estimated based on model for distribution and emissions [5], in reference to following groups of products: batteries, measuring and control equipment, light sources and other electrical and electronic equipment. About 9 Mg of mercury was launched to Polish market in mercury-containing products in 2008. The ban on placing mercury on market in fever thermometers and measuring devices intended for sale to the general was introduced in 2009. It will effect on reduction of mercury amount in products.

Mercury emission to air in period of first 10 years of use of products launched to market in base year was estimated as 0.46 Mg, see Table 1.

Table 1

Emission to air, recycling, safe storage and other places of mercury accumulation from mercury-containing products launched to Polish market in 2008 [6]

	In first year [Mg]	Within 10 years [Mg]
Emission to air	0.32	0.46
Recycling and safe storage of mercury	2.17	2.89
Landfilling of municipal wastes + mercury accumulated in products	6.90	6.04
Total	9.40	9.40

In this period 2.9 Mg of mercury contained in products will be collected selectively and then recycled or stored safely. Majority of mercury will get to municipal waste landfills, with problem of mercury release to water and soil, or will be still accumulated in products.

Emission to air from dental practice was also estimated. It is sum of emission from processes of old amalgam combustion in mass of infectious wastes from dental practice and emission from bodies cremation.

Essential problem is the use of amalgam fillings in dentist surgeries and clinics which entered into contracts with *National Health Fund* (NFZ) for cost-free services for public. Dental amalgam is now purchased in capsule form. Preparation of single filling needs making of excessive amount of prepared mixture in relation to real necessity. This excess is easily recollected as hazardous wastes. Old amalgam wastes are greater problem. Only the biggest parts of extracted old amalgam are collected to jars with water, reducing mercury evaporation, and separately delivered. Rest of extracted old amalgam deposited on single use filters on spittoons, get to mass of infectious wastes and is incinerated or get into sewage system.

For mercury emission to air from bodies cremation this value estimated for Poland is less significant than in west and north European countries. It results from cultural patterns and historical experience of Poland. Only 5 % of corpses were cremated in Poland in 2006, that causes share of mercury released in these processes is relatively low.

Annual consumption of 10 Mg of mercury for dental fillings in Poland results emission 1.45 Mg to air from combustion of displaced old amalgam in stream of infectious medical wastes. Mercury emission from dental fillings in creamation processes is 0.04 Mg.

National mercury emission to air from described sources was estimated for base year 2008 on level 17.7 Mg annually – see Fig. 1.

Main problem is emission from public power and heating plants. Second place have other industrial sectors, third – dental practice, and following places – commercial heating plants and households. The smallest participation in emission structure concerns mercury use in products.

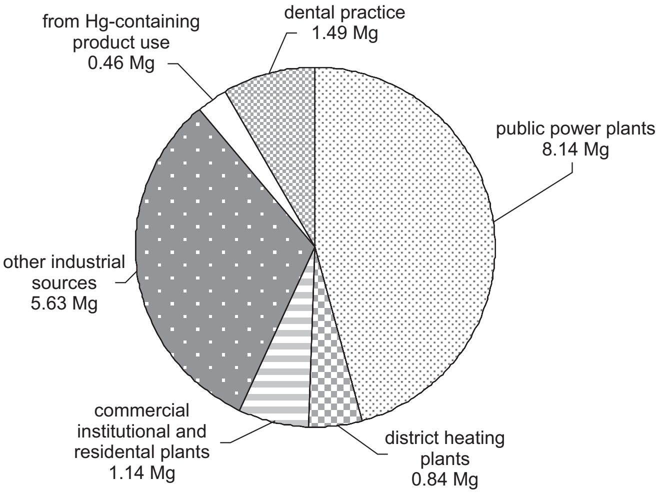

Fig. 1. Mercury emission to air in base year

Loads of mercury discharged to water and soil were estimated for large and medium industrial facilities together with its landfills (1.90 Mg), municipal waste water treatment plants in agglomerations above 100 thousand residents (1.07 Mg) and additionally for potential mercury release from municipal landfills (4.84 Mg) and dental amalgam in buried bodies (0.16 Mg). Total emission to air, water and soil in Poland was estimated as 25.7 Mg/year. This stream not covers re-emission of mercury before accumulated in environment.

Status Quo scenario

NILU Polska prepared also scenarios of mercury emission to atmosphere and loads discharged to water and soil to year 2020. In first scenario – Status Quo [4] – it was assumed that current practices and methods of mercury emission control from the end of 2008 will be maintained. This scenario is only comparative one. It is expected that in reality national and international pressure will cause actions leading to reduction of mercury emission.

Based on assumptions of project for Energy Policy of Poland from 2007, it was estimated that emission from industrial processes will increase (16.2 Mg) as result of increased coal consumption in power plants by 6 % and lack of significant changes in the other industrial sectors. Emission to air from mercury use in products (0.47 Mg) will be similar to emission in base year, because mercury consumption and waste management will not change. Predicted increase of mercury launched to market in batteries is exception. It is expected that average EU consumption factor (11 batteries per person) will be achieved in 2020.

Emission to air from dental practice (1.52 Mg) will change slightly in comparison with the base year considering the further use of amalgam in dentist surgeries and increase of cremated bodies to level 10 %. Total mercury emission to air for Status Quo scenario in 2020 will be 18.2 Mg annually.

For mercury discharges to water it was assumed that emission from industrial and municipal wastewater treatment plants (2.97 Mg) will not change in comparison with the base year. Potential releases of mercury from municipal landfills and dental fillings for Status Quo scenario will increase to 5.48 Mg annually. Finally total national anthropogenic emission to air, water and soil will increase from 25.7 Mg in base year 2008 to 26.6 Mg in 2020.

EXEC scenario

EXEC (*EXtended Emission Control*) scenario is the prognosis of economic growth continuation, assuming implementation of EU directives and international conventions [6]. Taken into account requirements of the IPPC directive 96/61/EC and BAT reference documents (BREFs), implementation of *best available techniques* for mercury emission reduction from industrial processes is expected. Changes to the IPPC directive are introduced by the new *Industrial Emission Directive* (IED) 2010/75/EU. This directive is a link between Large Combustion Plants directive (2001/80/EC) and directive on the incineration of waste (2000/76/EC). IED directive requirements will be in force since 1 January 2016. Demands of Poland extending transitory periods for large combustion plants to 30 June 2020 were taken into consideration. It concerns sources below 500 MW, for which the first permit was given before 27 November 2002 and which will prepare transitional national plans including limits of annual emissions. Exemptions from the obey of emission limit values – on condition that appropriate conditions are fulfilled – will be in force also for older power plants, combined heat and power plants as well as for heating plants below 200 MW until the end of 2023 at the longest.

EXEC scenario is based on projection of fuel consumption included in the final version of the “Energy Policy of Poland until 2030” [7]. In this projection until 2020, 28 % decrease of brown and hard coal consumption for power generation as well as 10 % decrease of coal consumption in district heating plants, residential sector and commercial plants is expected. BAT techniques will be implemented in energy sector, iron and steel production, non-ferrous metal production, cement production and chlorine production using mercury cell plants [8].

For fuel combustion processes implementation of primary methods for emission reduction as coal washing or fuel switching is expected. Coal-fired power plants will be equipped with secondary methods for emission reduction as *fabric filters* (FF) or *electrostatic precipitators* (ESP) operated in combination with *flue gas desulfurization* (FGD) techniques. Some power plants will be equipped with simultaneous control of SO_x, NO_x and mercury emission (catalytic methods), non-catalytic methods and techniques using sorbents.

In iron and steel production implementation of fine wet scrubbing systems and fabric filters together with carbon sorbents and then the use of catalytic oxidation is expected in sinter plants. Blast furnaces will be equipped with scrubbers and wet ESPs. Basic oxygen furnaces will be equipped with dedusting methods: dry ESPs and scrubbers as well as FFs or ESPs. For electric arc furnaces implementation of systems for dust collection and dedusting in FFs is predicted.

In projection for non-ferrous metal production it is expected implementation of best available techniques allowing to remove of mercury from process gases and to reduce of mercury amount which occurs during sulfuric acid production. Additionally high-effective FFs will be used. In copper production the use of modern FFs with burst-bag detectors and automatic filter cleaning system is recommended, whereas in lead and zinc production the use of combination of dry ESPs, wet scrubbers, mercury removal system and wet ESPs before sulfuric acid plants is recommended.

In cement production it is assumed that plants will be equipped with ESPs and FFs with burst-bag detectors and dust abatement techniques (minimization or prevention of fugitive dust emission). It is predicted that FGD techniques (wet scrubbers) will be used in many plants and some of plants will be also equipped with systems designed for heavy metals removal like activated carbon injection and dedusting.

Projection for chlorine production assumes the end of the mercury cell plants use as the mercury cells and asbestos diaphragm processes are not considered to be BAT and are significant source of mercury emission. Phase-out of mercury cells should eliminate problem of mercury emission in this sector. As a result of changes in production structure of particular sectors and implementation of proper methods for mercury emission reduction, predicted mercury emission from industrial processes will decrease to 6.1 Mg.

For mercury use in products 40 % reduction of mercury consuption for their production is expected. The ban on placing mercury on market in fever thermometers and measuring devices (eg manometers, barometers) intended for sale for public since 2009 results from directive 2007/51/EC. Other regulations define minimum collection rates for batteries and accumulators (45 % since 2016) and for electrical and electronic equipment (40 % for light sources and 24 % for other equipment). At the same time the increase of mercury-free button cell batteries production and fluorescent lamps share with low mercury content are expected.

Mercury emission to air in period of first 10 years of product use will decrease to 0.10 Mg, see Table 2. In this period 3.3 Mg of mercury contained in products will be recycled or stored safely. Smaller stream of mercury will get to municipal landfills or be still accumulated in products.

Table 2

Emission to air, recycling, safe storage and other places of mercury accumulation from mercury-containing products launched to Polish market in 2020 for EXEC scenario [6]

	In first year [Mg]	Within 10 years [Mg]
Emission to air	0.07	0.10
Recycling and safe storage of mercury	2.49	3.29
Landfilling of municipal wastes + mercury accumulated in products	2.84	2.01
Total	5.40	5.40

In case of dental practice mercury emission will decrease significantly (to 0.03 Mg), as result of the lower dental amalgam use and proper management of infectious wastes, incinerated in modern waste incineration plants.

It is assumed that suction systems and amalgam separators will be used in most dental surgeries, what allows to capture and treat it as a hazardous waste. Ceramic-polymer composites are alternative materials for dental fillings used for years, but their exclusive using in Poland would be more expensive for National Health Fund (NFZ). Another issue is a case of mercury emission from dental fillings resulting from bodies cremation hovewer it is less important in Poland in comparison with Western Europe.

At the same time it is expected that ten modern waste incineration plants will be operate in 2020: in Warsaw (with the annual capacity of 320 thousand Mg of wastes), in Silesian conurbation, Lodz, Gdansk-Gdynia conurbation and Krakow (each 250 thousand Mg), in Poznan (200 thousand Mg), in Szczecin and Bydgoszcz-Torun conurbation (each 180 thousand Mg), in Koszalin (120 thousand Mg) and Bialystok (100 thousand Mg).

Total mercury emission to air from industrial processes, mercury use in products and dental practice will achieve level 6.3 Mg – see Fig. 2. In emission structure, there will be a significant drop of the share of public power and heating plants, which will draw level with other industrial sectors.

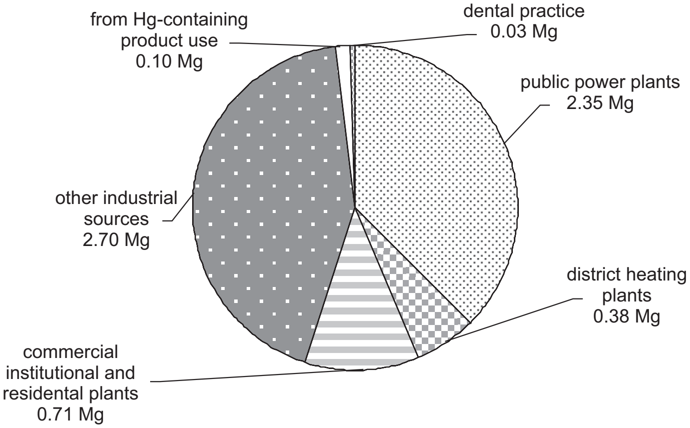

Fig. 2. Mercury emission to air in 2020 for EXEC scenario

For mercury loads discharged to water implementation of best available techniques is assumed, allowing decrease of emission from industrial processes to 0.87 Mg and decrease of emission from municipal waste water treatment plants to 0.49 Mg. Load of mercury gradually released from municipal landfills (1.22 Mg) will decrease significantly. It will be result of the smaller use of mercury in products and higher amount of modern waste incineration plants. Annual economic activities and consumer behavior will result the total anthropogenic mercury emission to the environment on level 8.9 Mg, what makes three-times drop of emission in comparison with the base year.

MFTR scenario

MFTR scenario is projection of *Maximum Feasible Technical Reduction* of mercury emission, in which additional mercury emission reduction measures will be applied in comparison with previous EXEC scenario [6]. Measures for mercury emission prevention (limitation of the use of mercury in products and its recycling as well as technological changes in industry).

In this scenario it is expected that power and heat production will still remain the main sources of mercury emission from industrial processes in Poland (2.81 Mg). Projection used in this scenario is based on 450 ppm scenario from IEA report [9], in which 24 % decrease of hard and brown coal consumption for power generation together with 50 % decrease of energy demand for purposes other than power generation are expected.

Until 2020 energy sector and other industrial sectors will be equipped in currently implemented emerging techniques, including techniques for heavy metals removal (activated carbon, sulfur impregnated sorbents and selenium impregnated filters). The share of coal combustion in pulverized boilers will decrease for fluidized bed combustion and clean coal technologies. In case of low-stack emission broaden switch from coal to gas and oil as well as the use of renewable energy sources and termomodernization of buildings are predicted.

In iron and steel production new iron-making techniques will be partially implemented – mainly direct reduction of iron ore. Scrap with controlled mercury content will be used as feedstock to basic oxygen furnaces. In non-ferrous metal production the use of chemical conversion methods of mercury and its compounds for mercury removal from process gases and produced sulfuric acid are proposed. The use of non-chemical methods allowing decrease of mercury amount in sulfuric acid is also recommended. The use of methods with selenium filter and selenium scrubber is considered as future solution.

In cement production it is assumed that all plants will be equipped with primary methods for emission reduction, abatement techniques for minimization of fugitive dust emission, dedusting techniques with the use of activated carbon and desulfurization technologies. In projection for chlorine production it is expected that all mercury using cell plants will be converted to membrane cells technology or to other mercury-free technologies.

Remaining sources of emission will have insignificant share in mercury emission structure. Slight use of mercury for production, only discharge lamps, will cause further drop of emission from mercury use in products (0.02 Mg), see Table 3. At the same time 0.8 Mg of mercury in products will be recycled or stored safely. Only 0.6 Mg of Hg will be landfilled or still accumulated in used products.

The ban on using amalgam in dental fillings will eliminate the problem of mercury emission from incineration of old amalgam with infectious wastes. Total mercury emission to air from industrial processes, mercury use in products and dental practice will equal 2.83 Mg – see Fig. 3. In comparison with EXEC scenario, further decrease of mercury emission to air is expected but emission structure will remain unchanged.

Table 3

Emission to air, recycling, safe storage and other places of mercury accumulation from mercury-containing products launched to Polish market in 2020 for MFTR scenario [6]

	In first year [Mg]	Within 10 years [Mg]
Emission to air	0.02	0.02
Recycling and safe storage of mercury	0.62	0.83
Landfilling of municipal wastes + mercury accumulated in products	0.77	0.55
Total	1.40	1.40

Loads of mercury discharged to water and soil will further decrease (to 0.45 Mg). Slight range of mercury use in products will cause that the potential gradual mercury release from municipal landfills (0.30 Mg) will significantly decrease. Annual economic activities and consumer behavior will result the total anthropogenic mercury emission to the environment on level 3.6 Mg, what makes seven-times drop of emission in comparison with the base year.

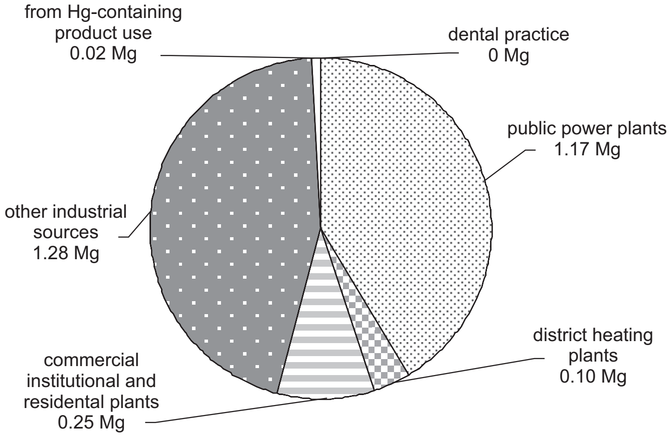

Fig. 3. Mercury emission to air in 2020 for MFTR scenario

Conclusions

It was estimated that mercury emission to air in base year 2008 was 17.7 Mg and total emission to air, water and soil was 25.7 Mg annually. In Status Quo scenario, growth of production and consumption will lead to the increase of mercury emission, see Fig. 4.

In EXEC scenario mercury emission to air will decrease to 6.3 Mg in year 2020 and total emission to air, water and soil to 8.9 Mg. This scenario is combination of measures oriented to mercury emission reduction (modern techniques of flue gas cleaning in industry, combustion of municipal and infectious wastes, technologies of wastewater

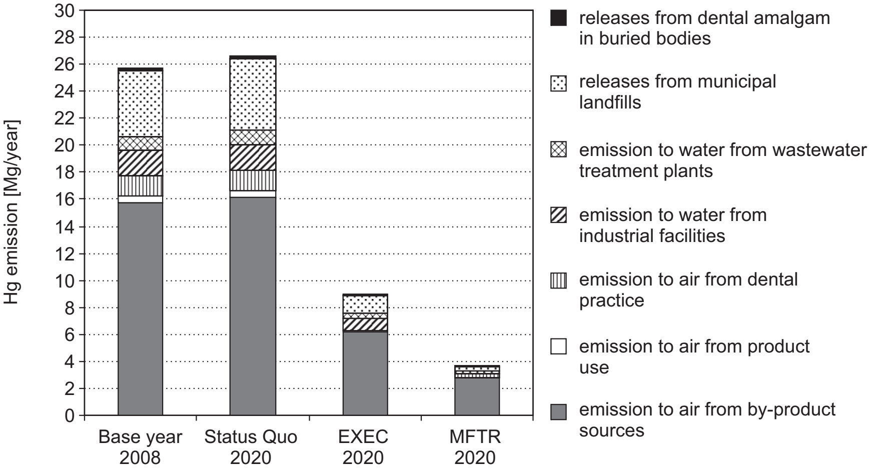

Fig. 4. Mercury emission to air, water and soil for particular scenarios

treatment) and strategies of emission prevention (reduction of coal consumption in energy sector, selective collection of mercury-containing product wastes and decrease of dental amalgam consumption).

In MFTR scenario mercury emission to air will achieve level 2.8 Mg Hg and total emission to environment – 3.6 Mg Hg annually. This scenario is most concentrated on cheaper strategies of emission prevention (ban on using mercury in batteries, electrical and electronic equipment, measuring and control equipment as well as in dental practice). Additional reduction of emission results from the use of emerging techniques.

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SCENARIUSZE EMISJI RTĘCI DO POWIETRZA, WÓD I GLEBY W POLSCE DO ROKU 2020

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Abstrakt: W 2005 r. Polska zajmowała czwarte miejsce wśród państw europejskich w emisji rtęci do powietrza, głównie z powodu spalania węgla kamiennego i brunatnego w energetyce. Zespół NILU Polska oszacował krajową emisję rtęci do powietrza oraz ładunki odprowadzane do wód i gleby dla roku bazowego 2008, a następnie przygotował scenariusze emisji rtęci do 2020 r. Inwentaryzacja emisji do powietrza objęła procesy przemysłowe, użytkowanie produktów zawierających rtęć i praktykę dentystyczną. Ładunki rtęci zrzucane do wód i gleby zostały oszacowane dla dużych i średnich zakładów przemysłowych, oczyszczalni ścieków komunalnych oraz dla potencjalnego uwalniania się rtęci ze składowisk odpadów komunalnych i z wypełnień dentystycznych w grzebanych zwłokach. W porównawczym scenariuszu Status Quo założono, że będą utrzymane bieżące praktyki i metody kontroli emisji rtęci, ale wzrost produkcji i konsumpcji będzie prowadzić do wzrostu emisji rtęci. W scenariuszu EXEC (zwiększonej kontroli emisji) emisja rtęci do powietrza spadnie z 17,7 Mg w roku bazowym do 6,3 Mg w 2020 r., a łączna emisja do powietrza, wód i gleby z 25,7 do 8,9 Mg. W scenariuszu MFTR (maksymalnej możliwej technicznie redukcji) emisja do powietrza osiągnie w 2020 r. poziom 2,8 Mg Hg, a łączna emisja do środowiska – 3,6 Mg Hg rocznie.

Słowa kluczowe: scenariusze emisji, rtęć, powietrze, woda, gleba

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Barbara BREZA-BORUTA[1]

BIOAEROSOLS OF THE MUNICIPAL WASTE LANDFILL SITE AS A SOURCE OF MICROBIOLOGICAL AIR POLLUTION AND HEALTH HAZARD

BIOAEROZOLE SKŁADOWISKA ODPADÓW KOMUNALNYCH JAKO ŹRÓDŁO MIKROBIOLOGICZNEGO ZANIECZYSZCZENIA POWIETRZA I ZAGROŻENIA ZDROWOTNEGO

Abstract: The aim of this study was to determine the composition of bacterial and fungal aerosol on the premises of the Municipal Waste Disposal Complex at Zolwin-Wypaleniska near Bydgoszcz and to evaluate the degree of microbiological air pollution at the appointed stands. Microbial concentration in the air was determined at the waste sorting station and in the active sector of the landfill site as well as in the point situated 200 m beyond the facility. It was found that the total number of bacteria in the air ranged from 10^2 to 10^4 cfu · m^{-3} and many times strong air pollution occurred on the premises of that facility. High concentration level of actinomycetes and indicator bacteria *Pseudomonas flourescens* contributed also to strong or moderate air pollution at research stands 1 and 2. Potentially pathogenic bacteria of the family *Enterobacteriaceae* (such as bacilli of *Salmonella* sp. and *Escherichia coli*) as well as faecal streptococci occurred in the largest amounts also at stands 1 and 2, and their number reached up to 10^3 cfu · m^{-3}. The obtained values show that both the sorting station the active sector of the waste landfill are serious emission sources of dangerous bacterial aerosol. They can pose a health hazard to the workers staying at those workstands. The determined amounts of fungal aerosol prove that it did not pose a microbiological hazard, and the studied air was described as moderately clean throughout the research period, only in the area of the sorting station it was polluted at several times. Among the isolated fungi, species of the genera *Aspergillus* and *Penicillium* predominated, as well as *Sclerotinia sclerotorum*. However, also potentially pathogenic species were detected in the studied air, such as: *Aspergillus fumigatus, Cladosporium herbarium*, *Alternaria alternata* etc. Their presence may affect the health of people (workers of the facility and residents of neighbouring areas) and the risk of the environmental pollution, since those species are well-known for their production of mycotoxins and inducing allergic reactions. Based on the registered concentrations of bacteria and fungi at the point 200 m away from the facility, it should be assumed that the studied air was not polluted and bioaerosol transmission from the sources of emission to the surrounding areas did not occur.

Keywords: airborne bacteria, airborne fungi, actinomycetes, bioaerosol, municipal waste landfill site

Working municipal waste landfill sites are assumed to be proecological facilities, but through emission of both chemical and biological pollutions they may have a negative

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effect on the state of the environment. Municipal facilities may affect surrounding soils, surface and ground waters, pollute the atmosphere and through the atmosphere, distant agricultural, urban and recreational areas [1–4]. Main agents polluting the air are chemical substances (odorogenic) and microorganisms (bioaerosols) [5, 6]. Emission of gases, dusts and bioaerosol at landfill sites occurs during waste transport, unloading and processing, at sorting stations and composting plants, which are very often situated on the premises of the facility [7, 8]. The basic difference between biological factors and other dangerous substances consists in the ability of the former to reproduce. Under favourable conditions, even a small number of microorganisms can considerably increase in a short time. Biological factors pose a very serious health hazard to people employed in public utilities. They constitute a crucial and still more appreciated problem of both occupational health care and the public health. It is estimated that at least several hundred million people in the world are exposed to the action of those agents. The majority of biological particles do not pose a health threat under the natural environmental conditions, but a part of them show pathogenic, allergenic or toxic properties. Biological factors highly differ in respect of a degree of infection risk. They include bacteria, fungi, viruses, protozoans and compounds excreted by microorganisms, such as: endotoxins, exotoxins, glucans, metabolites of fungi, mycotoxins, allergens etc [9–11].

In respect of the species composition of microorganisms contained in biological aerosol, we divide it into: saprophytic, infections and mixed, while none of them remains neutral for the environment. Live cells of biological aerosol often induce pathogenic infections, sometimes very serious, but also dead cells can provoke unfavourable health problems [12].

Both the knowledge of the bacterial and fungal composition, and also the level of concentration of bioaerosol particles in atmospheric air are essential for human health. Moreover, the fractional distribution of bioaerosol is a crucial element, since infections are caused by both a relatively high dose of large particles and a considerably smaller dose of small, submicronic particles. The respirable fractions, with the particle size up to 5 μm, is of particular importance in the epidemiology of infectious diseases, due to the easiness of spread and deep infiltrating the respiratory system, up to pulmonary alveoli [9, 13]. Contaminated air can be a cause of many illnesses. Depending on the composition of bioaerosol, it may cause occurring simple irritations and ailments, allergic reactions, infections, as well as dangerous infectious diseases and toxic reactions. The highest threat is posed by the components of bioaerosol transmitted by means of air – dust or air – droplet routes, which penetrate the organism through the skin, mucous membranes and food can also be the route of transmission [10].

Concentration of microorganisms in the environment of municipal waste landfill sites includes within a very wide range of values. Municipal wastes, and particularly their wet fraction, may contain bacteria, viruses, cysts of protozoans and eggs of worms, whose numbers can reach up to 10^9 per gram of wastes [14]. In the course of emptying cars transporting wastes, as well as their sweeping, compressing, closing sections, and sorting, bacteria and fungi spores are raised in the air. Gram-positive bacteria predominating among the determined bioaerosol belong to the genera: *Microccocus*, *Enterococcus*, S*taphylococcus*, *Bacillus*, *Mycobacterium*, whereas from Gram-negative bacteria: *Pseudomonas*, *Escherichia*, *Enterobacter* etc. [10, 14]. In the case of Gram-negative bacteria, produced enterotoxins and endotoxins occurring in their cell wall can cause various diseases (respiratory tract inflammation, toxic and allergic pneumonia). The presence of endotoxins in the air was observed at various workstations in the public utility facilities [9, 15]. For this reason, municipal waste landfill sites may be a potential source of many bacterial, viral or mycotic diseases for different organisms, the habitat of insects and rodents transmitting germs. Additionally, biological aerosol deriving from those facilities may contribute to pollution of nearby areas, as well as ground and surface waters [1, 16].

The aim of this study was to determine the quantitative and qualitative composition of the bioaerosol occurring on the premises and in the vicinity of the municipal waste landfill site. On the basis of the numbers of microorganisms, the level of microbiological pollution of atmospheric air was determined, which allowed the assessment of the level of health hazard at the appointed stands.

Material and methods

Location of sampling stands

The study of the bioaerosol composition was carried out at the Municipal Waste Disposal Complex Sp. z o.o. The facility is located at Zolwin-Wypaleniska, 4 km south from Bydgoszczy (Fig. 1). The Complex takes about 150 000 Mg (ton) of wastes yearly

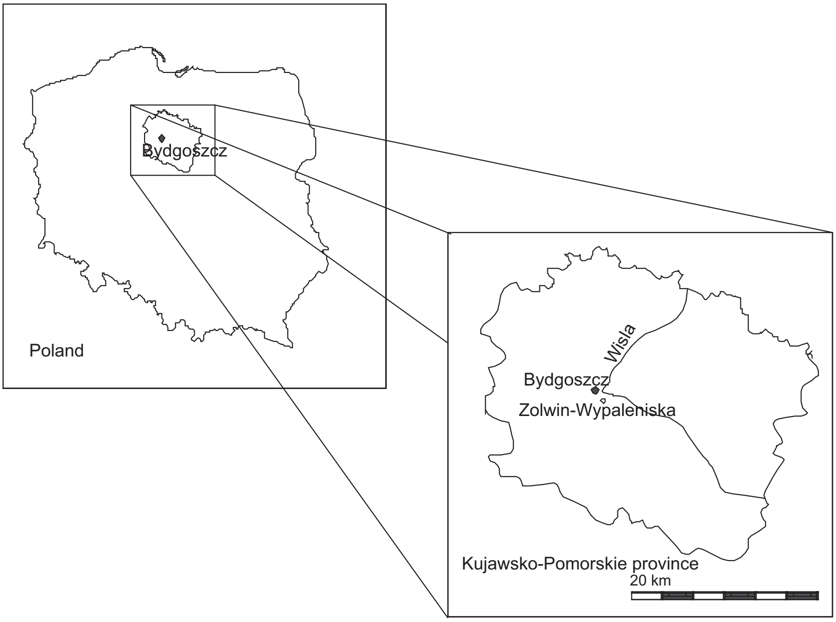

Fig. 1. Location of the studied area

from the city of Bydgoszcz, Solec Kujawski, communes Biale Blota and Nowa Wies Wielka. The wastes are partly neutralized and sorted. The Complex consists of three landfill sites, including one which is reclaimed (working in 1985–2003) and two working presently. The waste sorting station takes *ca* 50 thousand Mg (ton) of wastes. A total of 180 workers are employed in the facility [17].

Air samples were collected at three points, *ie*: in the area of the sorting plant (point 1), in the active sector of the waste landfill site (point 2) and at the point about 200 m to the east from the facility, in the vicinity of a housing estate (point 3). Analyses of the microbiological air pollution were made in the period from April to December 2008, taking into consideration the meteorological conditions prevailing in different times of the year.

Methods of the study

The air samples were taken with the impaction method using Microbiological Air Sampler MAS-100 Eco by Merck. Air samples were taken from the height of 1.5 m above the ground level. Through the head of the apparatus a strictly determined air volume was sucked on a Petri dish with agar medium, according to a season of the year and atmospheric conditions. The following groups of microorganisms were determined during the study, using the appropriate selective media:

– total number of bacteria on Standard nutrient agar (incubation 37 °C, 48–72 h),

– actinomycetes on the Pochon medium (28 °C, 7 days),

– bacteria *Pseudomonas fluorescens* on King B medium (26 °C, 48 h),

– mould and yeast-like fungi on wort agar (28 °C, 48–96 h),

– bacteria of the genus *Salmonella* on BPL agar media with brilliant green and phenol red acc. to Kauffmann (37 °C, 24 h),

– *Escherichia coli* and other bacteria of the family *Enterobacteriaceae* on ENDO agar with fuchsin and lactose (37 °C, 24 h),

– bacteria of the genus *Enterococcus* on agar with kanamycine, esculine and azide (37 °C, 24 h).

All the air measurements for the studied groups of microorganisms were made in four replications. The qualitative diagnostics of bacteria was conducted based on additional physiological and biochemical analyses. In the case of *E. coli* tests from the biochemical series IMViC were used, for *Salmonella* sp. A serological test with the polyvalent serum Hm. The final identification of faecal streptococci type – D was made using the serological Phadebact-test. Identification and determining the species composition of fungi were made based on mycological guidebook according to Gilman [18].

Concentration of microorganisms detected in the studied air was expressed as the number of colony-making units – cfu, per 1 m^3 of atmospheric air (cfu $\cdot$ m^{-3}). The results were worked out using a conversion table according to Feller for the air monitoring system MAS-100. The evaluation of the atmospheric air pollution level was performed according to the recommendation given in the Polish Standards: PN-89/Z-04111/02 and PN-89/Z-04111/03 [19, 20].

Results and discussion

The results of the study concerning the number of microorganisms and the degree of the atmospheric air pollution were presented in Tables 1–5.

Based on the obtained results, it was stated that microbiological air pollution occurred most frequently at the waste sorting station. The total number of bacteria at that stand in the period from April to November exceeded the values for strongly polluted air. Only in December their number fell, and the studied air was considered as moderately polluted. However, the highest value for the total number of bacteria was obtained at the place of waste disposal (54200 cfu $\cdot$ m^{-3}). At that point strong air pollution with total number of bacteria and with *P. fluorescens* remained in spring and summer months, whereas substantially fewer of them were isolated in autumn (Tables 1, 5).

The concentration of actinomycetes also remained on a very high level at the sorting station and strong air pollution occurred at as many as six times, and moderate pollution at the others. The maximal value of actinomycetes there amounted to 1984 cfu $\cdot$ m^{-3}. The air in the active sector of the landfill was strongly or moderately polluted with actinomycetes in all the research period. Indicator bacteria *Pseudomonas fluorescens* most frequently polluted the air at stand 1. The highest value, which amounted to 670 cfu $\cdot$ m^{-3}, was recorded in August at stand 2. Definitely fewer bacteria and actinomycetes was found at the point 200 m away from the facility. In the case of *P. fluorescens* a maximum 18 cfu was detected, whereas there were 84 cfu actinomycetes, and the total number of bacteria did not exceed 1095 cfu $\cdot$ m^{-3} (Table 1, 5). The obtained results for bacteria and actinomycetes indicate that they were not transmitted by air from the stands at which their very high concentration was observed to the area beyond the waste landfill limits.

Table 1

Concentration of selected groups of microorganisms in atmospheric air on the premises of Municipal Waste Disposal Complex and the surrounding area

Stand measurement	Term research [month]								
	IV	V	VI	VII	VIII	IX	X	XI	XII
	Total bacteria [cfu $\cdot$ m^{-3}]								
1*	15200	19373	12880	10673	24360	8775	10845	5028	1780
2	20287	54200	3340	6100	15200	1470	100	78	81
3	300	300	1095	660	138	135	330	330	133
Pseudomonas fluorescens [cfu $\cdot$ m^{-3}]									
1	62	180	430	174	110	73	105	25	34
2	204	87	70	134	670	15	10	2	10
3	7	10	12	18	0	17	2	0	2
Actinomycetes [cfu $\cdot$ m^{-3}]									
1	770	1633	1984	330	25	82	253	35	560
2	312	60	140	210	485	11	10	27	27
3	18	84	53	40	5	64	80	10	4

* Stand 1 – the waste sorting station, 2 – the active sector of the landfill site, 3 – 200m beyond the facility.

Each waste landfill site, even properly designed and operated, constitutes a source of pollution of the surrounding environment [20, 21]. The results of studies by local and foreign authors show that the atmospheric environment in the area of waste disposal is characterized by the occurrence of high concentrations of bacterial aerosol [6, 7, 23–25].

The highest concentration of bioaerosols in the area of the monitored the District Complex of Municipal Waste Disposal was recorded at the place where wastes were sorted and at the place of their deposition. Intensive car traffic, constant moving of vast heaps of impurities, increase the pollution of atmospheric air with microorganisms. Kocwa-Haluch et al [26] reported that irrespective of the time of the year, the total number of bacteria and fungi reaches the maximal values over the active landfill. Also the study carried out by Butarewic and Kowaluk-Krupa [27] at the municipal waste landfill site at Augustow indicated that the facility, in spite of properly managed operation, was a source of microorganism emission, both saprophytic ones and pathogenic towards the surrounding environment.

The high number of bacteria of the family *Enterobacteriaceae* and of faecal streptococci in the studied air turned out a potential health hazard to the workers of the monitored waste landfill site (Tables 2 and 3).

Table 2

The number of bacteria of the family *Enterobacteriaceae* in atmospheric air on the premises of Municipal Waste Disposal Complex and the surrounding area

Stand measurement	Term research [month]								
	IV	V	VI	VII	VIII	IX	X	XI	XII
	Escherichia coli [cfu · m^{-3}]								
1*	4	70	0	25	8	80	119	19	69
2	130	20	20	65	100	25	33	2	5
3	6	0	4	4	0	0	0	0	0
Salmonella sp. [cfu · m^{-3}]									
1	190	23	285	50	48	113	45	71	36
2	180	33	0	1	160	120	26	0	5
3	8	0	4	4	0	6	0	2	0
Other bacteria of the family *Enterobacteriaceae* [cfu · m^{-3}]									
1	18	1900	67	36	82	75	116	56	53
2	1740	30	54	78	155	22	45	0	8
3	10	20	12	3	0	6	0	0	2

* For a description, see Table 1.

Strong air pollution at the sorting station remained throughout the research period, whereas at the landfill in some months they were not found or there were substantially less of them than at stand 1. The highest value of *Enterococcus* sp. was obtained in May at the cap of the landfill, where 2800 cfu · m^{-3} was recorded. The number of bacteria of the family *Enterobacteriaceae* also stayed on a high level, in the case of *Escherichia coli* the maximal value amounted to 130, and in *Salmonella* sp. – 285 cfu · m^{-3}. High concentrations of faecal streptococci and bacteria of the family *Enterobacteriaceae* can affect deterioration in the sanitary state of the air and may pose a potential environmental hazard. However, it must be stressed that their number in the point appointed 200 m beyond the facility definitely decreased and did not exceed 20 cfu · m^{-3}. Based on those results, it may be concluded that a considerable emission of pathogenic bacteria from the source of their generating did not occur.

Table 3

The number of fecal streptococci in atmospheric air on the premises of Municipal Waste Disposal Complex and in surrounding area

Stand measurement	Term research [month]								
	IV	V	VI	VII	VIII	IX	X	XI	XII
1*	250	800	840	640	1250	1105	330	648	145
2	340	2800	12	20	160	245	115	2	2
3	2	0	0	6	0	4	0	0	4

* For a description, see Table 1.

Many authors [3, 14, 23, 28] indicate that the number of microorganisms getting to the air considerably decreases along with a distance from the emission source. This refers both to the total number of microorganisms and of bacteria not typical of the air, deriving from wastes. Both for bacteria of the family *Enterobacteriaceae* and faecal streptococci there are no threshold values determining the permissible content of those bacteria in the air. However, even their low concentration in the air may pose a potential hazard to the natural environment, as well as people and animal health.

Microorganisms making their way from the stored wastes into the air are subjected to numerous factors unfavourable to their development. Part of them die during several seconds, mainly due to drying, high temperatures, as well as because of the exceeding solar radiation. Only those microorganisms which are the most resistant and to the highest degree adopted to the unfavourable living conditions, retain their vitality long in the air [21, 29].

Fungi constitute an important fraction of bioaerosol. The vast majority of hyphal fungi and considerably less of yeast-like fungi were detected in the studied air. The obtained results show that also at the sorting station the air was most polluted with fungal bioaerosol, and the number of spores reached up to 53433 cfu · m^{-3}, whereas beyond the facility their amount definitely decreased and did not exceed the permissible level for the unpolluted air (Tables 4, 5). The determined concentration of fungi at the cap of the landfill indicated the moderately clean air, and the obtained values did not exceed 4000 cfu · m^{-3}. The species composition of air borne fungi is of great importance. The genera predominated among determined fungi included *Aspergillus* (*A. niger*), *Penicillium* (*P. notatum*), *Rhizopus* (*R. nigricans, R. oryzae*) as well as *Sclerotinia* (*S. sclrotorium*), whereas in smaller amounts were isolated *Epicoccum nigrum, Arthrinium phaespermum.* Moreover, potentially pathogenic species were identified, such as: *Aspergillus fumigatus Cladosporium herbarium*, *Alternaria alternata* Their presence in the air at the studied stands both at the facility and beyond the landfill can pose a health hazard to the workers and the residents of the surrounding areas, since those fungi excrete mycotoxins and induce allergic reactions.

Table 4

Concentration of moulds and yeast-like fungi in atmospheric air on the premises of Municipal Waste Disposal Complex and in surrounding area

Stand measurement	Fungi [cfu · m^{-3}]	Term research [month]								
		IV	V	VI	VII	VIII	IX	X	XI	XII
1[*]	moulds yeast-like	1924 0	3848 0	9175 50	3600 20	5900 1400	31310 0	53433 0	8901 0	15460 0
2	moulds yeast-like	427 287	854 0	690 50	600 40	3800 50	750 0	2070 0	65 0	879 0
3	moulds yeast-like	505 40	1010 0	360 10	4605 50	600 0	295 0	70 0	81 0	48 0

[*] For a description, see Table 1.

Table 5

Degree of microbial air contamination at research stands on the premises and in the vicinity of Municipal Waste Disposal Complex from April to December 2008, acc. to recommendations of PN [19, 20]

Month	Total bacteria			*Pseudomonas fluorescens*			Actinomycetes			Fungi		
	Stand measurement											
	1	2	3	1	2	3	1	2	3	1	2	3
IV	🟥	🟥	⬜	🟥	🟥	🟨	🟥	🟥	🟨	⬜	⬜	⬜
V	🟥	🟥	⬜	🟥	🟥	🟨	🟥	🟨	🟨	⬜	⬜	⬜
VI	🟥	🟥	🟨	🟥	🟥	🟨	🟥	🟥	🟨	🟨	⬜	⬜
VII	🟥	🟥	⬜	🟥	🟥	🟨	🟥	🟥	🟨	⬜	⬜	⬜
VIII	🟥	🟥	⬜	🟥	🟥	⬜	🟨	🟥	⬜	🟨	⬜	⬜
IX	🟥	🟨	⬜	🟥	🟨	🟨	🟨	🟨	🟨	🟥	⬜	⬜
X	🟥	⬜	⬜	🟥	🟨	🟨	🟥	🟨	🟨	🟥	⬜	⬜
XI	🟥	⬜	⬜	🟨	🟨	⬜	🟨	🟨	🟨	🟨	⬜	⬜
XII	🟨	⬜	⬜	🟨	🟨	🟨	🟥	🟨	⬜	🟥	⬜	⬜

🟥 heavily pollution 🟨 medium pollution ⬜ not pollution

Fungi are the predominating group in the air and they account for about 70 % of all microorganisms. More than 40000 species of fungi have been isolated so far [30]. Their common occurrence is determined by production of very numerous spores and modest nutritional and environmental demands [31–34]. Environmental pollution and threat connected with the presence of fungi in the air results from the fact that they can cause: allergies, asthma, broncho- and pulmonary mycoses and general infections. For example, *Aspergillus fumigatus* is responsible for more than 90 % pulmonary mycosis in people. Small sizes of conidia (2–3 μ) allow them to spread throughout the respiratory system [37]; whereas toxinogenic species of the genera *Aspergillus*, *Fusarium*, *Penicillium* etc may induce cytotoxic, neurotoxic, teratogenic and cancerogenic actions towards other organisms [9, 35–38].

Microclimatic conditions have a substantial effect on the number of microorganisms in the atmospheric air, which is confirmed with the studies by other authors [24, 31, 39]. The time of the year, climate and varied meteorological conditions have a decisive effect on the spread of pollutions in the atmosphere and the range of their effect on the natural environment and people [2, 5, 14]. Those relationships were noticeable in the author's study conducted both on the premises and beyond the facility. The numbers of microorganisms in the air, depends first of all on the temperature. The results of microbiological analyses proved that the largest pollution with bacteria occurred in the spring and summer period, whereas with fungi in the autumn months. Atmospheric air has limited abilities to self-cleaning, thus it is necessary to control its microbiological cleanliness, in order to reduce processes of its exceeding pollution.

An increase in the waste mass at landfill sites has a considerable effect on generating pollutions emitted to the atmosphere [40]. Many scientific studies and reports indicate the connection between the concentration of sub- and micronic particles making air pollutions and the state of health and mortality of populations exposed to inhaling this type of air [41–43].

Conclusions

1. The high level of the total numbers of bacteria, *Pseudomonas fluorescens* and actinomycetes was observed in atmospheric air at the determined stands at Municipal Waste Disposal Complex in Zolwin-Wypaleniska near Bydgoszcz, based on which the studied air was considered as strongly polluted in the spring and summer period.
2. Sorting station and the active sector of the landfill site turned out to be also serious emission sources of bacteria of the family *Enterobacteriaceae* (such as *Escherichi coli* and *Salmonella* sp.) as well as faecal streptococci.
3. Determined amounts of fungal aerosol indicates that it did not pose a microbiological threat and the studied air was described as moderately clean throughout the research period; only on the premises of the sorting station it was polluted at several times. However, among the isolated fungi some potentially pathogenic species were detected, such as: *Aspergillus fumigatus Cladosporium herbarium*, *Alternaria alternata*.
4. High concentration of potentially pathogenic bacteria and the presence of toxinogenic fungi in the air at the waste landfill site, proves a potential a health hazard to persons working as well as temporarily staying at that facility. Therefore, a proper protection should be created for workers exposed to the action of airborne biohazards.
5. Based on the low concentration of bacteria and fungi determined at the point 200 m away from the facility, it should be assumed that the studied air most often was not polluted there, and thus there was no bioaerosol transmission from the sources of emission, that is from the waste landfill and the sorting station, to the nearby areas.

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BIOAEROZOLE SKŁADOWISKA ODPADÓW KOMUNALNYCH JAKO ŹRÓDŁO MIKROBIOLOGICZNEGO ZANIECZYSZCZENIE POWIETRZA I ZAGROŻENIA ZDROWOTNEGO

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Abstrakt: Celem pracy było oznaczenie składu bioaerozolu bakteryjnego i grzybowego na terenie Zakładu Unieszkodliwiania Odpadów Komunalnych w Żółwinie-Wypaleniska koło Bydgoszczy oraz ocena stopnia mikrobiologicznego zanieczyszczenia powietrza na wyznaczonych stanowiskach. Koncentrację mikroorganizmów w powietrzu określano na terenie sortowni odpadów i w sektorze czynnym składowiska oraz w punkcie położonym 200 m poza obiektem. Stwierdzono, że liczba bakterii ogółem w powietrzu kształtowała się od 10^2 do 10^4 jtk $\cdot$ m^{-3} i doszło wielokrotnie do silnego zanieczyszczenia powietrza na terenie zakładu. Wysoki poziom koncentracji promieniowców i bakterii wskaźnikowych *Pseudomonas fluorescens* przyczynił się także do silnego lub średniego zanieczyszczenie powietrza na 1 i 2 stanowisku badawczym. Potencjalnie chorobotwórcze bakterie z rodziny *Enterobacteriaceae* (m.in. pałeczki *Salmonella* sp. i *Escherichia coli*) oraz paciorkowce kałowe w największych ilościach występowały również na stanowisku 1 i 2, a ich liczba dochodziła do 10^3 jtk $\cdot$ m^{-3}. Uzyskane wartości wskazują, że zarówno sortownia, jak i sektor czynny składowiska odpadów były poważnymi emitorami niebezpiecznego aerozolu bakteryjnego, zatem stanowić mogą zagrożenie zdrowotne dla pracowników przebywających na tych stanowiskach pracy. Oznaczona ilości aerozolu grzybowego świadczy, że nie stanowił on zagrożenia mikrobiologicznego, a badane powietrze określono jako przeciętnie czyste w całym okresie badawczym. Jedynie na terenie sortowni w kilku terminach doszło do jego skażenia. Wśród wyizolowanych grzybów dominowały gatunki z rodzaju *Aspergillus* i *Penicillium* oraz *Sclerotinia sclerotorum*. Jednakże wykryto w badanym powietrzu również gatunki potencjalnie chorobotwórcze, takie jak: *Aspergillus fumigatus Cladosporium herbarium*, *Alternaria alternata* i in. Ich obecność może wpływać na zdrowie ludzi (pracowników zakładu i mieszkańców przyległych terenów) oraz ryzyko skażenia środowiska, bowiem gatunki te znane są z produkcji mykotoksyn oraz wywoływania reakcji alergicznych. Na podstawie zarejestrowanego stężenia bakterii i grzybów w punkcie oddalonym 200 m od zakładu, należy przyjąć, że badane powietrze było niezanieczyszczone i nie doszło do przenoszenia bioaerozolu ze źródeł emisji na okoliczne tereny.

Słowa kluczowe: aerozol bakteryjny, aerozol grzybowy, promieniowce, bioaerozol, składowisko odpadów komunalnych

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EFFECT OF BOTTOM SEDIMENT SUPPLEMENT TO LIGHT SOIL ON THE CONTENT AND UPTAKE OF MACROELEMENTS BY MAIZE

WPŁYW DODATKU OSADU DENNEGO DO GLEBY LEKKIEJ NA ZAWARTOŚĆ I POBRANIE MAKROELEMENTÓW PRZEZ KUKURYDZĘ

Abstract: The aim of study was an assessment of supplement of a bottom sediment with grain size composition of clay to light soil on the concentrations and uptake of macroelements by maize. Bottom sediment applied as a supplement improving light soil properties was extracted from the Besko Reservoir (Sieniawskie Lake) in the Podkarpackie province. The bottom sediments were added to the soil in the 1st year of the investigations in the amount of 5, 10, 30 and 50 % of air-dried sediment in relation to dry soil mass. Bottom sediment added to soil had a positive influence on maize shoots biomass but only when applied in the smallest dose, *ie* 5 %. Applied bottom sediment positively affected maize chemical composition increasing the content and uptake of nitrogen, potassium, magnesium and calcium by maize. While utilizing bottom sediment in plant cultivation, one should take into consideration a necessity of application of supplementary PK fertilization due to low content of these elements both in the bottom sediment. Because of a high proportion of clay particles in its composition and alkaline reaction, bottom sediment may be applied as a supplement to light and acid soils to improve their properties, but only in small doses to 5 %. Bigger doses may be used for reclamation as a structure and soil forming material on soil-less grounds.

Keywords: bottom sediment, light soil, macroelements, maize

In some countries (Germany, The Netherlands, Belgium, Great Britain and USA) bottom sediments are extracted from river bottoms, retention reservoirs, channels, ports and ponds in order to maintain their navigability, improve retentive capacity and upgrade recreational and aesthetic values [1]. Because the phenomenon of silting up and shallowing of water reservoirs is inevitable, its seems rational to try utilising the parts of

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sediments which do not contain harmful amounts of heavy metals whereas their macroelements content may affect the quality of plants cultivated in the soil with bottom sediment supplement. The act on fertilizers and fertilization of 10 July 2007, does not cover bottom sediments as materials used for plant fertilization or improvement of soil fertility [2]. Bottom sediments are perceived as a material which may be used for agricultural purposes on condition that they meet the standards of soil quality on the site of their ultimate application, so their quality should be in compliance with the Decree of the Minister of the Natural Environment of 9 September 2002 [3].

If the material extracted from the bottom of silted up water reservoir poses no hazard for the environment, the environmentally justified method of such sediment management is its use as structure and soil forming material on soil-less grounds and wastelands [4–6]. Bottom sediments, particularly those revealing neutral or alkaline reaction and high content of silt and clay fractions may be used for improving light and acid soils productivity [7–9]. Numerous authors conducted research on their potential environmental and agricultural management [10–17].

Presented investigations aimed at an assessment of supplement of a bottom sediment with grain size composition of clay to light soil on the concentrations and uptake of macroelements by maize**.**

Material and methods

Bottom sediment applied as a supplement improving light soil properties was extracted from the Besko Reservoir (Sieniawskie Lake) in the Podkarpackie province (Fig. 1). The water reservoir consists of two parts: the main part on the Wislok River

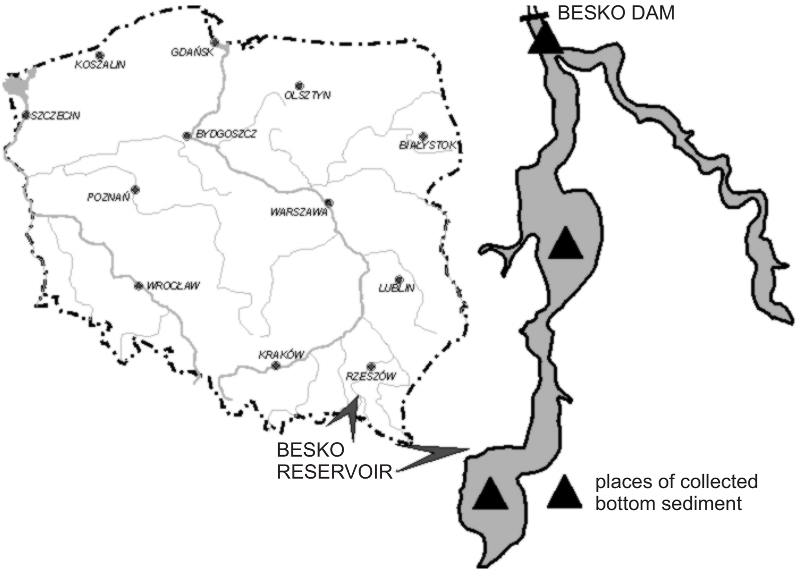

Fig. 1. Besko water reservoir and cross-sections of collected bottom sediments

with a capacity of *ca* 11 mln m^3 and a side part constructed on an inflowing Czernislawka stream with a capacity of *ca* 3 mln m^3. The channel type of the reservoir bowl is particularly noticeable on the side arm strongly cut into a rocky gorge. The main part of the reservoir forms a slightly wider Wislok River valley. Due to a decline in particle levitation force, the sedimentation process intensifies and two wide zones of the reservoir are especially prone to silting up. Changes (lowering) of impoundment level also contribute to formation of sandbanks or islands established by succession of terrestrial plants. Measurements of the reservoir conducted in 2006–2007 revealed a slight loss of its capacity [18, 19]. About 330 thousand m^3 of sediments became deposited in the side arm during the 28-year reservoir operation. Mean annual silting up of the Besko Reservoir expressed in capacity units does not exceed 0.01 hm^3 · year^{-1}. The sediment was sampled by means of Ekman sampler. In order to average the sampled material, 6 samples were collected from a given zone, mixed and the final averaged sample was formed. The sediment was collected from the 0–15 cm layer.

The pot experiment was conducted on a light soil with weak loamy sand grain size composition and slightly acid reaction (Table 1), which was enriched by a supplement of bottom sediment. The sediment was classified to a group of clay deposits with alkaline reaction, low content of bioavailable phosphorus and potassium (Table 1). Detailed characteristics of bottom sediments was presented in the paper of Baran et al [7].

Table 1

Selected properties of soil and bottom sediment

Component	% Share of ∅ [mm] fraction			pH KCl	C_{org}	N_{tot}	P_2O_5	K_2O
	1–0.1	0.1–0.02	< 0.02		[g · kg^{-1} d.m.]			
Soil	78	13	9	5.9	16.0	0.4	78.7	165.9
Bottom sediment	5	11	84	7.2	18.2	1.4	8.8	106.7

Heavy metal content in the analysed bottom sediments was shown in Table 2. Bottom sediment quality was determined on the basis of the Decree of the Minister of the Natural Environment of 16 April 2002 on the kinds and concentrations of substance which cause that the spoil is polluted [20], while the way of its management was determined on the basis of IUNG criterion [21] and Decree [3].

Table 2

Heavy metal content in bottom sediment

Bottom sediment	Zn	Cu	Ni	Cr	Cd	Pb
	[mg · kg^{-1} d.m.]					
	116.2	30.6	49.7	55.2	0.8	41.6
IUNG	I	0	I	I	0	0
Standard [15]	< 1000	< 150	< 75	< 200	< 7.5	< 200

In compliance with the above mentioned decree, heavy metal concentrations in the analyzed sediment did not exceed their content permissible for the soil [20]. According to IUNG assessment comprising a 6 degree soil classification with respect to heavy metal content and considering the reaction and grain size composition, the analysed material revealed natural concentrations of Cu, Pb and Cd but elevated content of Zn, Cr and Ni (Table 2). The bottom sediments were added to the soil in the 1st year of the investigations in the amount of 5, 10, 30 and 50 % of air-dried sediment in relation to dry soil mass. The same NPK fertilization, dosed respectively 1 gN, 0.4 gP and 1.1 gK per pot (6 kg of soil d.m.) was used in all objects. Mineral salts, as NH_4NO_3; KH_2PO_4 and KCl were added once prior to the test plant sowing. The test plant was maize (*Zea mays*), Bora c.v. The test plant was harvested after 70 days of vegetation. After harvest, the plant material was dried at 65 °C in a dryer with forced air flow and dry mass yield (shoots and roots) was determined. Subsequently the plant material was crushed in a laboratory mill and subjected to chemical analysis. Concentrations of Ca, K, P, Mg and Na were assessed in the plant material using ICP-EAS method after dry mineralization and dissolving the ash in HNO_3 (1:3). Nitrogen content was assessed by means of Kjeldahl's distilling method. Plant material was analysed in four simultaneous replications and a reference sample BCR 129 with known parameters was added to each series. The result was considered reliable if a *relative standard deviation* (RSD) did not exceed 5 %.The obtained results were elaborated statistically using one-way ANOVA, in Statistica 9.0 programme.

Results

Macroelements contents in maize shoots and roots were presented in Table 3. Sediment supplements to light soil caused a significant increase in nitrogen, potassium and calcium concentrations in maize shoot biomass in relation to the control. The highest content of nitrogen and potassium in the shoots was registered in the object with a 30 % supplement of bottom sediment, whereas calcium in the object with a 50 % admixture of bottom sediment (Table 3).

In comparison with the control, the increase reached respectively 40 % for nitrogen, 44 % for potassium and 52 % for calcium. Irrespectively of bottom sediment dose, a significant decline in phosphorus and sodium content, on average by 26 % and 20 % in comparison with the control, was noted in maize shoots. Magnesium content was not markedly dependent on the applied bottom sediment dose (Table 3). Content of the analysed macroelements, *ie* nitrogen, calcium, magnesium and sodium in roots was higher in the objects with bottom sediment supplement in comparison with the control (Table 3), however the dependence was statistically significant only for potassium and calcium. Like in the shoots, also in roots a bottom sediment addition diminished phosphorus content in roots. Assessment of the analyzed elements distribution in respective parts of maize evidenced higher contents of nitrogen, potassium, phosphorus and sodium in the shoot biomass in comparison with roots, whereas an opposite dependence was registered for calcium and magnesium (Table 3).

Table 3

Content of macroelements in maize

Treatment		$[g \cdot kg^{-1}$ d.m.]					
		N	K	Ca	Mg	P	Na
Soil	Sediment	Shoots					
100 %	0	8.7	15.0	2.0	1.9	2.0	1.0
95 %	5 %	11.6	16.5	3.1	2.3	1.4	0.9
90 %	10 %	11.5	16.5	3.3	2.1	1.4	0.7
70 %	30 %	14.5	21.6	3.9	2.2	1.5	0.7
50 %	50 %	12.0	19.4	4.0	1.9	1.7	0.9
$LSD_{0.05}$		*2.2*	*2.7*	*0.6*	*n.i.*	*0.2*	*0.2*
Soil	Sediment	Roots					
100 %	0	8.2	3.4	3.9	2.6	1.4	0.2
95 %	5 %	9.9	4.0	11.0	3.5	1.0	0.3
90 %	10 %	9.2	3.8	10.1	3.2	1.2	0.3
70 %	30 %	10.0	4.7	11.0	3.1	1.2	0.4
50 %	50 %	10.8	5.1	10.6	3.3	1.2	0.4
$LSD_{0.05}$		*n.i.*	*1.1*	*4.0*	*n.i.*	*n.i.*	*n.i.*

n.i. – statistically insignificant.

Maize yield considerably determined the content of studied macroelements. Significantly highest maize shoots and roots yields were demonstrated for the object with a 5 % admixture of bottom sediment (Table 4).

Table 4

Yield of maize

Treatment		Shoots	Roots	Total yield
Soil	Sediment	$[g \cdot pot^{-1}]$		
100 %	0	84.1^{bc}	17.4^{bc}	101.5^{bc}
95 %	5 %	92.0^{c}	18.2^{c}	110.2^{c}
90 %	10 %	77.5^{b}	12.5^{ab}	90.0^{b}
70 %	30 %	58.6^{a}	7.9^{a}	66.5^{a}
50 %	50 %	59.0^{a}	8.2^{a}	67.2^{a}
$LSD_{0.05}$		*8.9*	*3.3*	*9.4*

* homogenous gropus according to Tukey test; $\alpha < 0.05$.

The investigations demonstrated that the applied doses of bottom sediment over 5 % diminished the amount of obtained maize biomass. In the objects with 30 or 50 % doses of bottom sediment, the yield of maize shoots diminished about 1.5-fold and roots yield over twice in comparison with the control and the object with a 5 % bottom sediment supplement. However, as was previously demonstrated, the biggest content of studied macroelements in maize was registered in these objects. It may be explained by a concentration of the element content due to application of 30 and 50 % sediment doses. A fact of considerable reduction of root mass in the objects with 30 and 50 % supplement of bottom sediment (Table 4) also deserves attention. It may be surmised that introducing such big amounts of bottom sediment with grain size composition of clays to light soil unfavourably affected a change of air conditions in the formed substratum, *ie* soil became too clumped and compacted.

The amount of macroelements taken up with maize yield depended on the crop yield and a given element concentration (Table 3 and 4). The uptake of individual macroelements by maize (shoots + roots), depending on the experimental object was presented in Fig. 2. Total macroelements uptake per pot fluctuated as follows: 0.87–1.07 gN; 1.18–1.39 gK; 0.23–0.39 gCa; 0.14–0.23 gMg, 0.09–0.19 gP and 0.05–0.09 gNa · pot^{-1}.

The highest nitrogen, potassium, calcium and magnesium removal was noted in the object with a 5 % supplement of bottom sediment (Fig. 2), however for potassium this dependence was not statistically significant. It should be noticed, that all applied doses

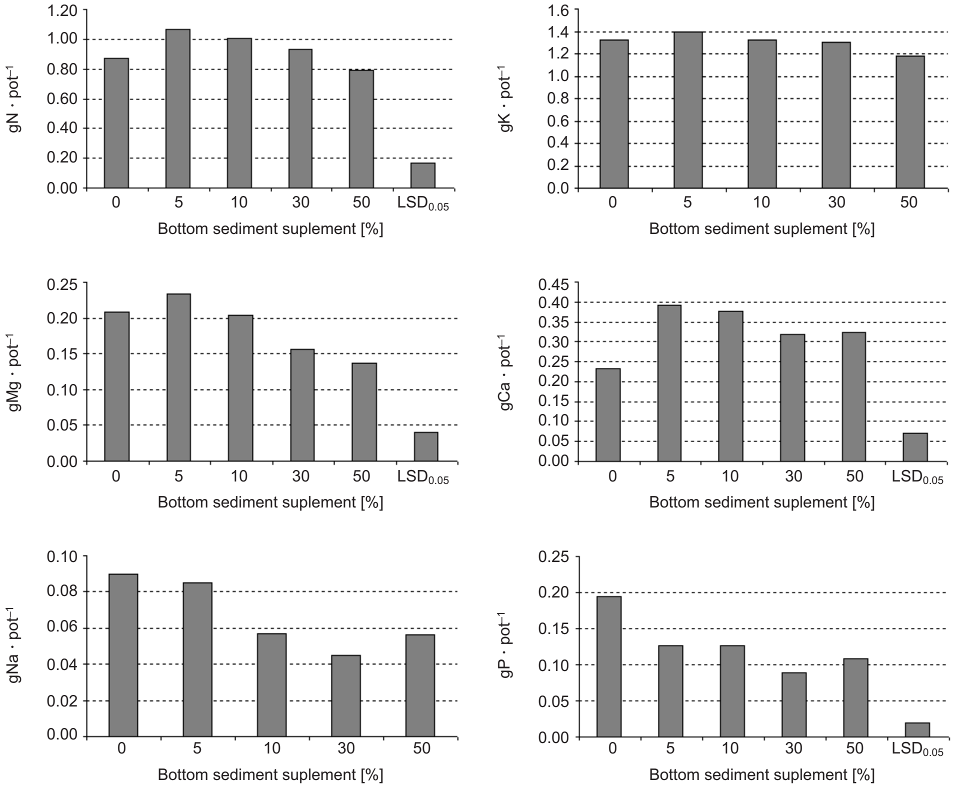

Fig. 2. Uptake of macroelements by maize

of bottom sediment markedly affected an increase in calcium uptake by maize, respectively between 28 and 40 % in comparison with the control. The investigations demonstrated that applied bottom sediment doses influenced a decreased uptake of phosphorus and sodium by maize in comparison with the control. In relation to the control, plants in the objects with a bottom sediment supplement absorbed from 1.5 to over twice less of phosphorus and sodium. Moreover, a tendency was noticed that high doses of bottom deposits, *ie* 30 and 50 % cause a decline in the uptake of all studied macroelements by maize, which is connected with an unfavourable effect of these doses on this plant yields (Table 4). Irrespectively of the sediment share in soil, the uptake of analyzed macroelements by maize shoots was higher than by roots. The structure of the above-mentioned elements uptake by the plant shows that maize shoots absorbed respectively between 5 and 11-times more of nitrogen; from 21 to 34 times more of potassium; from 7 to 10 times more of phosphorus and from 1 to 2 times more of magnesium; between 2 and 3 times bigger amounts of calcium and between 13 and 27 times more of sodium.

An important measure of plant chemical composition are interrelations between minerals. As has been demonstrated by numerous studies, the optimal proportions are: Ca : P (2 : 1); Ca : Mg (2.0 : 3.1); K : (Ca + Mg) (1.6 : 2.2); K : Mg (6 : 1) and K : Ca (2 : 1) [22]. Macroelements interrelations in maize shoots were presented in Table 5.

Table 5

Macroelements interrelations in maize shoots

Treatment		Ca : P	Ca : Mg	K : (Ca + Mg)	K : Mg	K : Ca
Soil	Sediment					
100 %	0	1.0	1.0	1.2	7.7	7.6
95 %	5 %	2.3	1.3	1.4	7.0	5.3
90 %	10 %	2.3	1.5	1.5	7.8	5.1
70 %	30 %	2.9	1.8	1.5	10.2	5.5
50 %	50 %	2.4	2.2	1.4	10.4	4.8

Ca : P ratio in maize dry mass in the objects with 5 % and 10 % share of bottom sediments assumed values close to optimal (Table 5). The highest Ca : P ratio was noted in maize in the objects with a 30 % admixture of bottom sediment, whereas the control plants had too low value of this ratio, therefore it may be presumed that bottom sediment added to the soil improved the quality of obtained plant biomass. Ca and Mg antagonism is commonly known, so the optimal ratio of these macroelements in plants should fluctuate between 2 and 3 : 1. The value of Ca : Mg ratio in the test plants was lower than the stated optimum in the objects with 5 % and 10 % sediment supplement and approximate to optimal proportion in the objects with 30 % and 50 % share of bottom sediments (Table 5). However, like in case of Ca : P ratio, the control plants had very low Ca : Mg ratio, therefore bottom sediment added to the soil improved the quality of obtained plant biomass. An important criterion of an assessment of plant mineral composition is the relationship K : (Ca + Mg) and its value should not exceed 2.2.

From the perspective of the obtained biomass utilisation for animal feed, plants from all experimental treatments revealed approximate to optimal value of this ratio. Bottom deposit applied to light soil affected a considerable widening of K : Mg and K : Ca ratios in maize. Undoubtedly, a low content of potassium in maize shoot biomass noted in the presented experiment and relatively high contents of calcium and magnesium (Table 3) caused an unfavourable change of the relationship between the above-mentioned macroelements.

Applied bottom sediment dredged from the Besko Reservoir revealed a big share of clay fractions in its composition and alkaline reaction, also its heavy metal concentrations did not exceed the contents permissible for the soil, for soil or group and land in B group [3]. Therefore, it may be applied as a supplement to light, acid soils in order to improve their productivity. A positive effect of bottom deposit supplement on biomass production was observed in the discussed experiment and the highest maize yield was obtained in the object with the lowest dose of bottom deposit, *ie* 5 %. Bigger doses of bottom sediment caused a depression of crop yield caused by the unfavourable air conditions in the formed substratum.

Similar results were obtained in the investigations on the environmental use of bottom sediment dredged from the Roznow Reservoir (Malopolska Region) [23]. The authors stated that the sediment supplement to very acid soil favourably affected the amount of produced plant biomass. In the quoted investigations the highest doses of the sediment, between 14 and 16 % caused an apparent decline in crop yields [23]. Fonesca et al [12, 13] revealed a positive influence of substrata prepared from soil and bottom sediments from the Maranhao and Monte Novo (Portugal) Reservoirs while investigating their effect on growth and development of tulips and pepper. Investigations conducted by other authors also focused on sediment admixture to soil effect on chemical composition of plants [15, 17]. Presented investigations demonstrated that increasing proportion of bottom sediment in light soil influenced an increase in the content of potassium, calcium, nitrogen and magnesium in maize shoot biomass but a decrease in phosphorus and sodium concentrations. Rahman et al [15] demonstrated that bottom sediments originating from fish ponds may be a potential source of nitrogen, phosphorus and potassium for forage crops. The author demonstrated that the sediment from fish ponds supplied to plants about 62 % N, 67 % of bioavailable P and 64 % of bioavailable K. According to literature [22] the optimal nutrient concentrations in maize at 8 leaves stage have been assumed as: 30–50 gN; 3.0–6.0 gP; 30–45 gK; 2.0–6.0 gMg and 3.0–10 gCa $\cdot$ kg^{-1} d.m. In the presented investigations maize shoot biomass in the objects with bottom sediments from the Besko reservoir revealed deficient concentrations of nitrogen, potassium and phosphorus but the optimal content of magnesium and calcium (Table 3).

Conclusions

1. Bottom sediment added to light soil had a positive influence on maize shoots biomass but only when applied in the smallest dose, *ie* 5 %. Bigger doses of the sediment caused a depression in maize crop yield.

2. Applied bottom sediment positively affected maize chemical composition increasing the content and uptake of nitrogen, potassium, magnesium and calcium by maize. However, the plant shoot biomass did not meet the animal feed quality criteria because of too low concentrations of nitrogen, phosphorus and potassium.

3. While utilizing bottom sediment in plant cultivation, one should take into consideration a necessity of application of supplementary PK fertilization due to low content of these elements both in the bottom sediment and maize yield.

4. Because of a high proportion of clay particles in its composition and alkaline reaction, bottom sediment may be applied as a supplement to light and acid soils to improve their properties, but only in small doses to 5 %. Bigger doses may be used for reclamation as a structure and soil forming material on soilless grounds.

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WPŁYW DODATKU OSADU DENNEGO DO GLEBY LEKKIEJ NA ZAWARTOŚĆ I POBRANIE MAKROELEMENTÓW PRZEZ KUKURYDZĘ

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Abstract: Celem badań była ocena wpływu dodatku osadu dennego o składzie granulometrycznym iłu do gleby lekkiej na zawartość i pobranie makroelementów przez kukurydzę. Osad denny zastosowano jako dodatek poprawiający właściwości gleby lekkiej, wydobyto z dna zbiornika Besko (jez. Sieniawskie) w woj. podkarpackim. Osady denne dodano do gleby w I roku prowadzenia badań w ilości 5, 10, 30 i 50 % osadu powietrznie suchego w stosunku do suchej masy gleby. Osad denny dodany do gleby lekkiej miał pozytywny wpływ na plon biomasy kukurydzy, ale tylko w najmniejszej dawce, tj. 5 %. Zastosowany osad denny wpłynął pozytywnie na skład chemiczny kukurydzy, zwiększając zawartość i pobranie przez kukurydzę azotu, potasu, magnezu i wapnia. Wykorzystując osad denny w uprawie roślin, należy zwrócić uwagę na konieczność zastosowania uzupełniającego nawożenie mineralnego PK, z powodu niskiej zawartości tych pierwiastków w osadzie dennym. Badany osad denny ze względu na duży udział w jego składzie części ilastych, zasadowy odczyn może być stosowany jako dodatek do gleb lekkich i kwaśnych w celu poprawy ich właściwości jednak w niewielkich dawkach do 5 %. Większe dawki osadu mogą być stosowane w rekultywacji jako materiał strukturo- i glebotwórczy na grunty bezglebowe.

Słowa kluczowe: osad denny, gleba lekka, makroelementy, kukurydza

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EFFECT OF LIMING AND APPLICATION OF SLUDGE ON THE CONTENT OF NITROGEN AND CARBON IN TEST PLANTS AND IN SOIL IN A FOUR-YEAR POT EXPERIMENT

WPŁYW WAPNOWANIA I OSADU ŚCIEKOWEGO NA ZAWARTOŚĆ AZOTU I WĘGLA W ROŚLINACH TESTOWYCH I W GLEBIE, W CZTEROLETNIM DOŚWIADCZENIU WAZONOWYM

Abstract: The aim of the study was to determine the effect of liming and applying varied doses of sludge (10, 20 and 40 % of fresh mass relative to the weight of soil in a pot) on the content of nitrogen and carbon in plants and in soil, in a four-year pot experiment. Italian ryegrass (*Lolium multiflorum*) was used as the test plant in the first year, maize and silage sunflower in the second and third years and Italian ryegrass again in the fourth year. The total nitrogen and carbon content was determined in soil samples, taken after each harvest, by the elemental analysis method using a CHN autoanalyser. The nitrogen and carbon content in the test plants cultivated on the soil in limed pots was found to be lower than, or comparable with, those cultivated without liming. The highest content of nitrogen was found in Italian ryegrass cultivated in the first year of the experiment, fertilised with sludge, while the highest content of carbon was in maize cultivated in the second and third year. The highest content of carbon was found in unlimed soil in the second year (more so after the sunflower harvest than after maize harvest) and the highest nitrogen content was found in limed soil in the first year of the experiment. The experiment found a positive effect of consequent action of sludge on the content of carbon and nitrogen in the soil of fertilised pots.

Keywords: nitrogen, carbon, test plants, soil, sludge, liming

Nitrogen is one of the fundamental elements, essential for the proper growth and development of plants. It also affects soil fertility and plant yield [1–5]. The taking up and use of the macroelement by plants, introduced to the soil with sludge or in the form of other organic materials, depends mainly on the soil property, agritechnical and humidity conditions and on the plant species. Evaluation of the sludge utility for

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fertilisation is supplemented by determination of its effect on soil [7]. A number of papers have shown the effect of fertilisation on quantitative and qualitative transformations of organic matter in soil [8–11]. The humus-forming value of organic matter depends on the carbon content in it which, in turn, determines the susceptibility of organic compounds to mineralisation and transformation into humic compounds [12]. Czekala [13], Kalembasa et al [14] have shown that sludge introduces large amounts of organic carbon to soil, while the organic compounds contained in it are not readily soluble.

The aim of the study was to determine the effect of liming and applying varied doses of sludge on the content of nitrogen and carbon in test plants and in soil, in a four-year pot experiment.

Material and methods

A pot experiment was conducted during four vegetation seasons in the years 2001–2004 in a greenhouse. This random experiment was conducted in triplicate. Each pot was filled with 10 kg of soil taken from the humus horizon, with the granulometric composition of light loamy sand (acc. to PTG), with $pH_{KCl} = 4.19$, total nitrogen content $0.980\ g \cdot kg^{-1}$, total organic carbon $11.3\ g \cdot kg^{-1}$, available phosphorus and potassium: 1.00 and $1.15\ mg \cdot kg^{-1}$.

Before filling the pots, the soil was sifted through a 1 cm mesh sieve and divided into two parts. One was limed with $CaCO_3$ according to Hh = 1 and left for a month while humidity was maintained at 50–60 % of the maximum water capacity. Thus prepared, the soil was poured into the pots, which resulted in obtaining two series: I – no liming (unlimed soil), II – with liming (limed soil). Subsequently, fresh sludge was introduced to the pots, from communal sewage from the wastewater treatment plant in Siedlce, after methane fermentation, in the amount of 10, 20 and 30 % relative to the soil weight, and mixed thoroughly. The deposit contained $41.5\ g \cdot kg^{-1}$ of nitrogen, $351\ g \cdot kg^{-1}$ of carbon in dry matter; dry matter accounted for 24.5 % of the whole. The chemical composition of the sludge suggested its utility in plant fertilisation [15].

Sludge was applied on a one-off basis 10 days before seeding of Italian ryegrass (in the first year of the experiment). The following were introduced in a sludge dose of 10 % (g per pot): C – 85.9, N – 10.2. The soil humidity in the pots was maintained at 50–60 % of the maximum water capacity.

The following were used as test plants: in the first year – Italian ryegrass (*Lolium multiflorum* Lam.), cultivar Kroto, harvested in four re-growths (cuts), at 30-day intervals; in the second and third years – maize, cultivar Nimba, which was harvested after 75 days of vegetation, and silage sunflower, sown after maize was harvested (into the same pots) and harvested after 70 days of vegetation. In the fourth year, Italian ryegrass was used, harvested as in the first year. One g of grass or 5 seeds of maize or sunflower were sown into each pot; after germination, three plants (maize or sunflower) were left in each pot.

The total nitrogen and carbon content was determined in plant and soil samples taken after each harvest, by the elemental analysis method, using a CHN autoanalyser, manufactured by Perkin Elmer.

The results were worked out statistically; the significance of the differences between average values was evaluated with an analysis of variance (the calculations were made with FR Analvar 3.2 software); when the differences were significant, the $LSD_{0.05}$ values were calculated according to Tukey's test.

Results and discussion

The factors analysed in the four-year pot experiment (liming, fertilisation with sludge) differentiated the content of carbon and nitrogen in test plants (Italian ryegrass in the first and fourth years, maize and sunflower in the second and third year) (Table 1–3).

Carbon content in the plants biomass varied depending on the plant species; throughout the experiment, ranging from 343 $g \cdot kg^{-1}$ (in the first re-growth of Italian ryegrass in the fourth year) to 442 $g \cdot kg^{-1}$ (in maize, in the second year). More carbon was found in Italian ryegrass in the first year (average 413 $g \cdot kg^{-1}$) than in the fourth year (average 390 $g \cdot kg^{-1}$) of the experiment; more in maize biomass (average of two years 430 $g \cdot kg^{-1}$) than in sunflower (average of two years 401 $g \cdot kg^{-1}$).

The average carbon content in biomass of the analysed plants during the four year slightly varied between the pots with unlimed soil (410 $gC \cdot kg^{-1}$; the lowest content – in the pots fertilised with the smallest dose of sludge 399 $g \cdot kg^{-1}$) and where lime was added (408 $gC \cdot kg^{-1}$). Significantly more carbon was found in the pots where 20 % and 30 % of sludge was added (average 416 $g \cdot kg^{-1}$) than in ones where 10 % of sludge was added (399 $g \cdot kg^{-1}$).

Of the plants cultivated in the experiment, the highest content of carbon was found in the biomass of maize (average 435 $g \cdot kg^{-1}$ on unlimed soil and 437 $g \cdot kg^{-1}$ on limed soil in the 2nd year of the experiment; in the 3rd year – 427 and 421 $g \cdot kg^{-1}$, respectively), followed by the biomass of sunflower in the 3rd year (407 and 400 $g \cdot kg^{-1}$, respectively), Italian ryegrass in the 1st year (413 and 414 $g \cdot kg^{-1}$, respectively), sunflower in the 2nd year (397 and 399 $g \cdot kg^{-1}$, respectively), and the lowest content was in Italian ryegrass in the 4th year (401 and 388 $g \cdot kg^{-1}$, respectively). A similar content of nitrogen and carbon in grass fertilised with sludge has been reported by Siuta [16].

Chemical analysis revealed that the nitrogen content was higher in the biomass of Italian ryegrass (especially in the 1st year of the experiment – average of 40.8 $g \cdot kg^{-1}$ in unlimed pots and 39.6 $g \cdot kg^{-1}$ in limed ones; in the 4th year: 19.0 and 17.0 $g \cdot kg^{-1}$, respectively) than in sunflower biomass (average in the 2nd year: 14.6 and 13.7 $g \cdot kg^{-1}$, respectively, and in the 3rd year: 12.1 and 11.9 $g \cdot kg^{-1}$, respectively) and maize (average in the 2nd year: 10.2 and 9.49, and in the 3rd year 6.44 and 6.28 $g \cdot kg^{-1}$, respectively). Mazur et al [2005] report a similar content of nitrogen in meadow sward, ranging from 14.0 to 30.0 $gN \cdot kg^{-1}$ of dry matter. This is mainly a consequence of the genetic properties of the test plants and their yield [17].

Liming significantly affected nitrogen content in test plants in the 1st, 2nd and 3rd year of the experiment (for maize). Fertilisation with sludge significantly affected nitrogen content in the plants, significantly more so in the unlimed pots. The content of the element increased with an increasing dose of sludge as compared with the control in all the years of the experiment. Many authors have confirmed the beneficial effect of sludge on yielding and nitrogen content in crops [18, 19].

Table 1

The content of carbon and nitrogen [$g \cdot kg^{-1}$] in Italian ryegrass in first year in the pot experiment

Fertilization	C	N	C : N	C	N	C : N	C	N	C : N	C	N	C : N	Mean	
	I cut			II cut			III cut			IV cut			C	N
Soil no liming														
Control object	401	19.0	21.1	419	21.7	19.3	410	26.1	15.7	411	38.9	10.6	410	26.4
10 %	409	52.9	7.74	413	45.1	9.17	407	45.9	8.86	413	48.1	8.58	411	48.0
20 %	415	54.1	7.67	417	42.7	9.76	420	46.8	8.98	419	47.7	8.79	418	47.8
30 %	413	51.3	8.05	409	34.9	11.7	416	40.3	10.3	417	45.9	9.09	414	43.1
Mean	410	44.3	11.4	415	36.1	12.5	413	39.8	11.0	415	45.2	9.27	413	40.8
Soil liming														
Control object	408	20.8	19.6	414	21.1	19.6	421	21.8	19.3	419	29.8	14.1	416	23.3
10 %	412	52.0	7.92	414	47.3	8.75	416	40.7	10.2	422	35.4	11.9	416	43.9
20 %	416	53.4	7.79	410	46.8	8.75	416	37.2	11.2	420	44.8	9.37	415	45.6
30 %	401	50.0	8.02	409	43.7	9.35	411	43.4	9.47	414	45.4	9.09	409	45.6
Mean	409	44.1	10.8	412	39.7	11.6	416	35.8	12.5	419	38.9	11.1	414	39.6

	C	N
	First year of experiment	
$LSD_{0.05}$ for: A – for liming, B – for fertilization, C – for cuts B/A; A/B; C/A; A/C; C/B; B/C – interaction	A = 0.197 B = 0.368 C = 0.368 B/A = 0.521 A/B = 0.395 C/A = 0.521 A/C = 0.395 C/B = 0.737 B/C = 0.737	A = 0.192 B = 0.359 C = 0.359 B/A = 0.508 A/B = 0.384 C/A = 0.508 A/C = 0.384 C/B = 0.718 B/C = 0.718

10 %, 20 %, 30 % – of waste activated sludge to the mass of soil.

Table 2

The content of carbon and nitrogen [$g \cdot kg^{-1}$] in maize and sunflower, in second and third year in the pot experiment

Fertilization	C	N	C : N	C	N	C : N	C	N	C : N	C	N	C : N
	second year of experiment						third year of experiment					
	maize			sunflower			maize			sunflower		
Soil no liming												
Control object	426	6.10	69.9	403	11.4	35.4	427	5.67	75.4	399	10.4	38.4
10 %	434	10.1	43.0	396	11.6	34.1	420	5.95	70.6	405	10.8	37.5
20 %	439	9.75	45.0	390	13.1	29.8	435	7.10	59.9	415	11.4	36.4
30 %	440	15.0	29.4	398	22.3	17.8	426	7.05	60.5	409	15.9	25.7
Mean	435	10.2	46.8	397	14.6	29.3	427	6.44	66.5	407	12.1	34.5
Soil liming												
Control object	440	6.30	69.9	396	12.4	32.0	417	5.65	73.8	399	11.1	35.9
10 %	442	7.80	56.7	393	10.2	38.6	422	6.60	64.0	411	10.8	38.1
20 %	428	9.95	43.1	405	12.9	31.4	415	6.10	68.1	391	11.2	34.9
30 %	439	13.9	31.6	403	19.1	21.1	429	6.75	63.6	398	14.3	27.9
Mean	437	9.49	50.3	399	13.7	30.8	421	6.28	67.4	400	11.9	34.2

$LSD_{0.05}$ for:	Second year of experiment			
	maize		sunflower	
	C	N	C	N
A – for liming, B – for fertilization, B/A; A/B – interaction	A = n.s. B = 5.06 B/A = 7.16 A/B = 5.16	A = 0.622 B = 1.22 B/A = 1.73 A/B = 1.24	A = n.s. B = n.s. B/A = n.s. A/B = n.s.	A = 0.436 B = 0.857 B/A = 1.21 A/B = 0.872
	Third year of experiment			
	A = 2.16 B = 4.24 B/A = 5.99 A/B = 4.31	A = 0.146 B = 0.287 B/A = 0.406 A/B = 0.292	A = 2.67 B = 5.25 B/A = 7.43 A/B = 5.35	A = n.s. B = 0.879 B/A = 1.24 A/B = 0.895

n.s.– non significant difference.

Table 3

The content of carbon and nitrogen [g · kg^{-1}] in Italian ryegrass in fourth year in the pot experiment

Fertilization	C	N	C : N	C	N	C : N	C	N	C : N	C	N	C : N	Mean	
	I cut			II cut			III cut			IV cut			C	N
Soil no liming														
Control object	403	13.3	30.3	410	17.6	23.3	374	17.4	21.5	392	17.3	22.7	395	16.4
10 %	416	14.7	28.3	400	18.1	22.1	360	15.7	22.9	391	16.2	24.2	392	16.2
20 %	419	21.6	19.4	403	20.6	19.6	410	20.1	20.4	391	17.2	22.9	406	19.9
30 %	431	27.2	15.9	407	23.1	17.6	399	23.1	17.3	411	20.2	20.3	412	23.4
Mean	417	19.2	23.5	405	19.9	20.7	386	19.1	20.5	396	17.7	22.5	401	19.0
Soil liming														
Control object	408	13.1	31.2	384	15.5	24.8	395	18.2	21.7	398	15.4	25.8	396	15.6
10 %	353	13.1	27.0	398	16.8	23.2	390	19.1	20.4	376	17.5	21.5	377	16.6
20 %	343	16.0	21.4	399	17.8	22.4	385	19.5	19.7	400	18.2	22.0	382	17.9
30 %	395	17.5	22.6	402	15.9	25.3	392	19.8	19.8	394	18.5	21.3	396	17.9
Mean	375	14.9	25.6	394	16.5	23.9	391	19.2	20.4	392	17.4	22.7	388	17.0
LSD$_{0.05}$ for: A – for liming, B – for fertilization, C – for cuts B/A; A/B; C/A; A/C; C/B; B/C – interaction					C					N				
					Fourth year of experiment									
					A = n.s. B = 30.9 C = n.s. B/A = n.s. A/B = n.s. C/A = 43.7 A/C = 33.1 C/B = n.s. B/C = n.s.					A = n.s. B = 0.407 C = 0.217 B/A = 0.576 A/B = 0.433 C/A = n.s. A/C = 33.1 C/B = 0.433 B/C = 0.576				

n.s.– non significant difference.

The C : N ratio in the test plants was affected by varied content of nitrogen (Table 1–3). The ratio was the broadest in maize in unlimed pots – 29.4–75.4 : 1; on limed pots – 31.6–73.8 : 1; in sunflower it was equal to 17.8–38.4 : 1 and 21.1–38.6, respectively; in Italian ryegrass, the average of regrowths in the 1st year was 8.56–15.5 and 8.97–17.9, respectively, and in the 4th year it was 17.6–24.1 and 21.1–25.4, respectively. The C : N ratio was narrower in pots fertilised with 30 % of sludge and broader in control pots.

When evaluating the fertilising value of sludge, an important feature is the ability to provide plants with nutrients, which is shown in the element content in the test plant biomass. Based on this assumption, Fig. 1 shows the changes in nitrogen and carbon content for the test plant species. The values refer to Italian ryegrass in the 4th year as compared with the 1st year of the experiment and for maize and sunflower in the 3rd year as compared with the 2nd year. The largest decrease in nitrogen content was observed in biomass of Italian ryegrass (over 50 %), followed by maize (about 35 %) and the smallest decrease was in sunflower (about 15 %). Liming also increased the nitrogen content decrease rate. The carbon content in test plants was also decreased by soil liming as compared with soil without liming. The largest decrease in carbon content was observed in Italian ryegrass – about 4 % on average, followed by maize (3 %) and the carbon content in sunflower increased by about 2 % compared with the 2nd of the experiment.

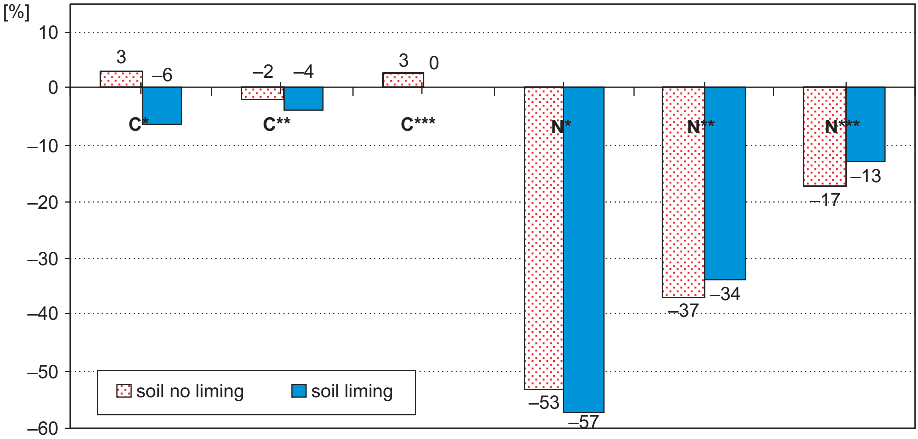

Fig. 1. Changes [%] total nitrogen and carbon in the biomass of the test plants: C* – changes the contents of C in Italian ryegrass, in the fourth year, compared with the year of the study; C** – changes the content of C in maize, in the third year, compared with the second year of the study; C*** – changes to the content of C in the sunflower, in the third year, compared with the second year of the study; N* – changes the content of N in Italian ryegrass, in the fourth year, compared with the year of the study; N** – changes the content of N in maize, in the third year, compared with the second year of the study; N*** – changes the content of N in the sunflower, in the third year, compared with the second year of the study.

The carbon content in the soil after the four-year experiment ranged from 6.40 g · kg^{-1} (after sunflower harvest, in the 2nd year) to 25.8 g · kg^{-1} (after harvesting the first regrowth of Italian ryegrass, in the 4th year) (Table 4–6). Liming significantly differentiated carbon content in the soil after the test plants were harvested, except in

Table 4

The content of carbon and nitrogen [g · kg $^{-1}$] in soil in first year in the pot experiment

Fertilization	C	N	C : N	C	N	C : N	C	N	C : N	C	N	C : N	Mean	
	I cut			II cut			III cut			IV cut			C	N
Soil no liming														
Control object	11.2	0.985	11.4	11.1	0.988	11.2	11.2	1.12	9.96	11.9	1.19	9.99	11.4	1.07
10 %	11.9	1.90	6.27	11.9	2.54	4.69	12.8	2.15	5.96	12.6	2.36	5.33	12.3	2.24
20 %	13.6	2.90	4.68	12.5	2.89	4.32	13.8	2.78	4.97	15.3	2.99	5.10	13.8	2.89
30 %	14.9	2.15	6.95	14.9	3.15	4.74	14.1	3.02	4.66	14.1	3.59	3.92	14.5	2.98
Mean	12.9	1.98	7.33	12.6	2.39	6.24	13.0	2.27	6.39	13.5	2.53	6.09	13.0	2.10
Soil liming														
Control object	11.3	1.02	11.1	11.2	1.03	10.9	12.6	2.03	6.20	12.6	1.23	10.2	11.9	1.33
10 %	12.0	2.75	4.37	12.2	2.58	4.71	14.1	3.02	5.06	13.5	2.15	6.27	13.0	2.63
20 %	13.5	2.98	4.67	12.9	2.98	4.45	15.0	3.14	4.77	13.4	3.48	4.52	13.7	3.15
30 %	14.1	2.20	6.39	15.0	3.36	4.44	14.1	3.14	4.48	14.1	3.14	4.48	14.3	2.96
Mean	12.7	2.24	6.63	12.8	2.49	6.13	13.6	2.34	5.13	13.4	2.50	6.37	13.1	2.39
LSD$_{0.05}$ for: A – for liming, B – for fertilization, C – for cuts B/A; A/B; C/A; A/C; C/B; B/C – interaction					C					N				
					First year of experiment									
					A = n.s.; B = 0.571; C = 0.571; B/A = n.s; A/B = n.s.; C/A = n.s.; A/C = n.s.; C/B = 1.14; B/C = 1.14					A = 0.030; B = 0.056; C = 0.056; B/A = 0.079; A/B = 0.059; C/A = 0.079; A/C = 0.059; C/B = 0.112; B/C = 0.112				

n.s.– non significant difference.

Table 5

The content of carbon and nitrogen [$g \cdot kg^{-1}$] in soil, in second year in the pot experiment

Fertilization	C	N	C : N	C	N	C : N	C	N	C : N	C	N	C : N
	Second year of experiment						Third year of experiment					
	maize			sunflower			maize			sunflower		
Soil no liming												
Control object	15.5	1.80	8.61	6.50	0.701	9.27	8.30	0.900	9.22	7.50	0.710	10.6
10 %	17.8	1.90	9.37	23.0	2.70	8.52	12.8	1.30	9.85	16.4	1.50	10.9
20 %	17.9	2.00	8.95	23.9	2.80	8.54	14.4	1.60	9.00	13.2	1.70	7.76
30 %	15.4	1.80	8.56	19.7	2.00	9.85	18.6	2.10	8.86	18.4	1.90	9.68
Mean	16.7	1.88	8.87	18.3	2.05	9.05	13.5	1.48	9.23	13.9	1.45	9.74
Soil liming												
Control object	9.30	1.10	8.45	6.40	0.80	8.00	9.80	1.00	9.80	7.60	0.700	10.7
10 %	19.4	2.30	8.43	17.8	1.90	9.37	10.4	1.20	8.67	17.2	1.40	12.3
20 %	16.4	3.20	5.13	13.3	1.60	8.31	20.6	2.20	9.36	15.8	1.80	8.77
30 %	11.3	3.10	3.65	19.5	2.10	9.29	19.4	2.10	9.24	18.1	1.81	10.1
Mean	14.1	2.43	6.42	14.3	1.60	8.74	15.1	1.63	9.27	14.7	1.43	10.5

LSD$_{0.05}$ for: A – for liming, B – for fertilization, B/A; A/B– interaction	Second year of experiment			
	maize		sunflower	
	C	N	C	N
	A = 0.360; B = 0.707; A/B = 0.720; B/A = 1.00	A = 0.270; B = 0.531; A/B = 0.541; B/A = 0.751	A = 0.697; B = 1.37; A/B = 1.39; B/A = 1.94	A = 0.150; B = 0.300; A/B = 0.305; B/A = 0.424
	Third year of experiment			
	A = 0.294 B = 0.577 A/B = 0.588 B/A = 0.816	A = n.s. B = 0.380 A/B = n.s. B/A = n.s.	A = 0.496 B = 0.976 A/B = 0.992 B/A = 1.38	A = n.s. B = 0.453 A/B = n.s. B/A = n.s.

n.s. – non significant difference.

Table 6

The content of carbon and nitrogen [$g \cdot kg^{-1}$] in soil, in fourth year in the pot experiment

Fertilization	C	N	C : N	C	N	C : N	C	N	C : N	C	N	C : N	Mean	
	I cut			II cut			III cut			IV cut			C	N
Soil no liming														
Control object	10.5	1.00	10.5	9.70	1.00	9.70	11.0	1.10	10.0	15.0	1.50	10.0	11.6	1.20
10 %	20.6	2.20	9.36	12.1	1.30	9.31	9.70	1.10	8.82	17.1	1.70	10.1	14.9	1.58
20 %	19.9	2.10	9.48	19.1	2.10	9.10	13.7	1.70	8.06	17.2	1.71	10.1	17.5	1.90
30 %	21.4	2.10	10.2	18.7	2.30	8.13	16.8	1.90	8.84	18.2	1.80	10.1	18.8	2.03
Mean	18.1	1.85	9.89	14.9	1.68	9.06	12.8	1.45	8.93	16.9	1.68	10.1	15.7	1.68
Soil liming														
Control object	11.8	1.10	10.7	11.1	1.00	11.1	8.40	1.00	8.40	15.8	1.50	10.5	11.8	1.20
10 %	25.8	2.70	9.56	13.0	1.30	10.0	10.6	1.20	8.83	17.4	1.80	9.67	16.7	1.75
20 %	15.7	1.80	8.72	18.3	1.00	18.3	16.3	1.80	9.06	17.9	1.10	16.3	17.:1	1.43
30 %	20.8	2.30	9.04	22.6	2.40	9.42	15.9	1.80	8.83	18.3	1.30	14.1	19.4	1.95
Mean	11.8	1.15	9.51	16.7	1.75	12.2	17.1	1.43	8.87	19.4	1.95	12.6	16.3	1.57
$LSD_{0.05}$ for: A – for liming, B – for fertilization, C – for cuts, B/A; A/B; C/A; A/C; C/B; B/C – interaction					C					N				
					fourth year of experiment									
					A = 0.239 B = 0.450 C = 0.450 B/A = 0.636 A/B = 0.478 C/A = 0.636 A/C = 0.478 C/B = 0.900 B/C = 0.900					A = 0.088 B = 0.166 C = 0.166; B/A = 0.234 A/B = 0.176 C/A = 0.234 A/C = 0.176 C/B = 0.331 B/C = 0.331				

the first year of the experiment. The carbon content in unlimed (13.0 g · kg^{-1}) and limed soil (13.1 g · kg^{-1}) in the 1st year of the experiment was comparable, although in the second year there was more in limed than in unlimed soil and more after sunflower harvest than after maize harvest. Significantly more carbon was found in limed soil in the 3rd and 4th year of the experiment compared with unlimed soil, after maize harvest (15.1 and 13.5 g · kg^{-1}), respectively; after sunflower harvest (14.7 and 13.9 g · kg^{-1}) respectively, and after Italian ryegrass harvest (16.3 and 15.7 g · kg^{-1}), respectively.

Fertilisation with sludge significantly differentiated the carbon and nitrogen content in soil after the test plants were harvested. Carbon and nitrogen content in limed and unlimed soil was found to increase with an increasing dose of sludge, especially in the 1st, 3rd and 4th year of the experiment. More carbon and nitrogen was found in unlimed soil, fertilised with 10 and 20 % of sludge after maize and sunflower harvest than in soil fertilised with 30 % of sludge. The largest amount of nitrogen (nearly three times more than in the control) was found in soil after harvesting Italian ryegrass in the 1st year of the experiment, following the largest application of sludge. This is a consequence of the large amount of the element introduced with sludge.

Figure 2 shows the percentage changes of nitrogen and carbon content in limed and unlimed soil in the 1st, 2nd and 3rd year of the experiment. Carbon content in the 2nd year of the experiment increased as compared with the 1st year: in limed soil it increased by about 35 % and in unlimed soil by 8 %. The values in the 3rd year changed: in unlimed soil it decreased by over 20 %, while in limed soil it increased by 5 %. The carbon content in the 4th year of study increased by 15 and 9 %, respectively, as

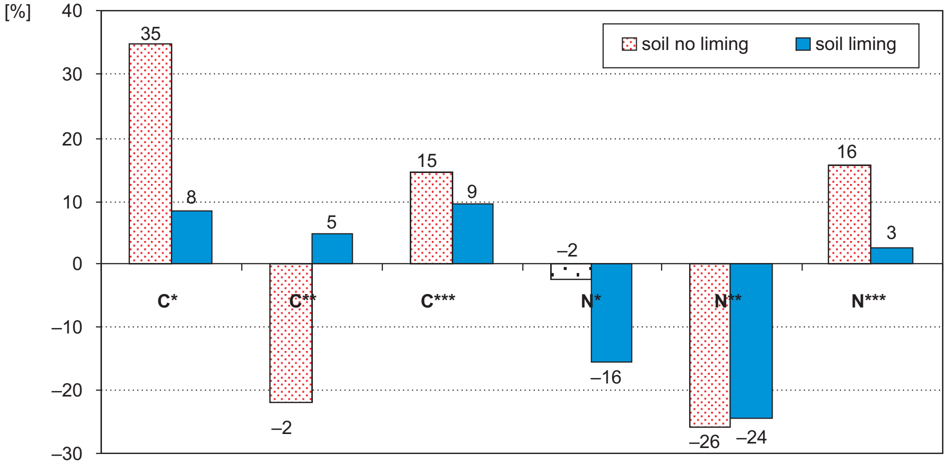

Fig. 2. Changes [%] total nitrogen and carbon in the soil, in the following years experience: C* – changes the contents of C in soil, in the second year compared with the first year of the experiment; C** – changes the contents of C in soil, in the third year compared with the second year of the experiment; C*** – changes the contents of C in soil, in the fourth year compared with the third year of the experiment; N* – changes the contents of N in soil, in the second year compared with the first year of the experiment; N** – changes the contents of N in soil, in the third year compared with the second year of the experiment; N*** – changes the contents of N in soil, in the fourth year compared with the third year of the experiment.

compared with the previous year. The total nitrogen content decreased in the 2nd and 3rd years of the experiment; in the 4th year it increased and there was more in unlimed soil (16 %) than in limed soil (3 %).

Studies conducted by many authors [20–26] have confirmed the significant role played by sludge in restoring carbon resources in agricultural land. Baran et al [22] observed a more beneficial effect of sludge than that of manure on carbon content. Kalembasa et al [14], Kalembasa and Wysokinski [2] reported on the high fertilising value of sludge, which is higher than that of manure in terms of the crop yield.

Conclusions

1. A varied content of carbon and nitrogen was found in test plants in a four-year pot experiment. The highest content of nitrogen was found in Italian ryegrass cultivated in the first year of the experiment, fertilised with sludge, while the highest content of carbon was in maize cultivated in the second and third year.
2. The nitrogen and carbon content in the test plants cultivated on the soil in limed pots was found to be lower than, or comparable with, those cultivated without liming.
3. The broadest C : N ratio was found in maize, followed by silage sunflower and Italian ryegrass.
4. The experiment found a positive effect of the consequent action of sludge on the content of carbon and nitrogen in the soil of fertilised pots. The highest content of carbon was found in unlimed soil in the second year, more so after sunflower harvest than after maize harvest, while the highest nitrogen content was found in limed soil in the first year of the experiment.

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WPŁYW WAPNOWANIA I OSADU ŚCIEKOWEGO NA ZAWARTOŚĆ AZOTU I WĘGLA W ROŚLINACH TESTOWYCH I W GLEBIE, W CZTEROLETNIM DOŚWIADCZENIU WAZONOWYM

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Abstrakt: Celem pracy było zbadanie wpływu wapnowania i zróżnicowanych dawek osadu ściekowego (10, 20 i 30 % św. m. w stosunku do masy gleby w wazonie) na zawartość azotu i węgla w roślinach i glebie, w czteroletnim doświadczeniu wazonowym. Rośliną testową w I roku doświadczenia była życica wielokwiatowa, w II i III roku kukurydza i słonecznik pastewny, w IV roku ponownie życica wielokwiatowa. W próbkach roślinnych i glebowych, pobieranych po każdym zbiorze roślin, badano ogólną zawartość azotu i węgla metodą analizy elementarnej, na autoanalizatorze CHN. W roślinach testowych uprawianych na glebie obiektów wapnowanych stwierdzono mniejszą bądź porównywalną zawartość azotu i węgla niż w roślinach uprawianych bez wapnowania. Najwięcej azotu zanotowano w życicy wielokwiatowej uprawianej w I roku doświadczenia, nawożonej osadem ściekowym, najwięcej węgla w kukurydzy uprawianej w II i III roku. Największą zawartość węgla stwierdzono w glebie bez wapnowania, w II roku, więcej po zbiorze słonecznika niż kukurydzy, największą zawartość azotu w glebie wapnowanej, w I roku eksperymentu. Przeprowadzone badania wykazały korzystny wpływ następczego działania osadu ściekowego na zawartość węgla i azotu w glebie obiektów nawozowych.

Słowa kluczowe: azot, węgiel, rośliny testowe, gleba, osad ściekowy, wapnowanie

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CONTENT OF HEAVY METALS IN MEADOW SOILS IN DIFFERENT SEASONS

ZAWARTOŚĆ METALI CIĘŻKICH W GLEBACH ŁĄKOWYCH W RÓŻNYCH PORACH ROKU

Abstract: The content of heavy metals like cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu) and nickel (Ni) was investigated in the meadow soils in the district of Bochnia in autumn and winter season 2010/2011. The meadows were located at different distances from the road 2 m, 100 m and 200 m. The soils tested showed an average pH of acidic to nearly neutral and humidity in autumn 17.17–29.53 % and in winter season within 24.68–37.59 %. Statistically significant showed differences in the content of Zn, Cu, Ni and Pb between stations in the autumn and winter seasons. In relation to cadmium did not show such dependence. The content of this element (0.6–0.88 ppm) is similar occurred at all stations, regardless of the season. The number and diversity of pedofauna were also analyzed, which was higher in the winter season in the studied meadow soils. It has been found, however, that significant differences in metal content did not affect the abundance of soil fauna at different stations in the studied seasons.

Keywords: heavy metals, meadow soils, pedofauna, density, diversity.

Processes in the soil are essential for the sustainability and productivity of terrestrial ecosystems. Anthropogenic activity causes major changes in the circulation of elements in the environment, leading to contamination of its individual components. The problem of soil pollution is very significant as it may indirectly or directly affect adversely the human health. Particularly serious is heavy metal soil contamination due to the occurrence of their migration and accumulation, also in plants of permanent farmland situated along traffic routes, which is exacerbated with growing numbers of internal combustion vehicles [1]. The soil pollutants may enter the human body indirectly through ingestion of plants that were taking up harmful components from the polluted soil or were contaminated by atmospheric deposition of particles from industrial

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emissions or from wind or rainwash erosion. Physical and chemical properties of the soil affect the take-up of elements by plants and their absorption into the food chain system. Among them, it is the pH value that matters most for the accumulation of heavy metals in plants. In an acidic environment, plants may take up great amounts of these elements, particularly Cd, Zn and Ni, even from lightly polluted soils [2, 3]. In the soil environment, heavy metals are characterised by varying mobility. Lead and nickel are less mobile, while Cd and Zn are the most mobile.

Lead is strongly bound by the organic matter of the surface soil layer and slightly migrates deeper into the profile. The mobility of nickel in soils depends on the granulometric and mineralogical structure of the soil. Nickel is strongly bound by mineral colloids and iron hydroxides, and therefore its movement is limited. Cadmium displays high mobility in the environment and is easily taken up by plants. The total content of metals in the soil is determined, next to the size of the deposition, by the humification conditions of the plant material and the balance of accumulation and leaching processes of the metals [3, 4].

The goal of the performed investigations was to determine the heavy metal (Pb, Cd, Ni, Zn and Cu) content of the soil at three meadow sites located at the distance from 2 to 200 m from a main traffic route in the autumn and winter seasons, as well as to determine the effect of the studied metals on the density of soil fauna found there.

Materials and methods

Cadmium, lead, zinc, copper and nickel contents of meadow soils were investigated in Bochnia County in the autumn and winter seasons of 2010/2011. The meadows were situated at various distances, 2 m, 100 m and 200 m from a busy county road No. 1444 k. The contents of selected heavy metals in the soil were determined by FAAS (after prior mineralisation of the tested soil material). Soil samples were taken from the test sites by means of a 25 cm × 25 cm soil frame from a surface of 1 m^2 and then, mesofauna were flushed out by a dynamic method in a modified Tullgren apparatus. The effect of the heavy metal content on the pedofauna population numbers was also analysed. The moisture content and the pH value of the investigated soil was also determined.

The results were analysed using a unifactorial ANOVA variance procedure. The *post hoc analysis* was performed by means of the Tukey's HSD test. Furthermore, Pearson's and r^2 coefficients of correlation between the heavy metal concentration and the population of the studied fauna were analysed. The differences were statistically significant at $p < 0.05$.

Results and discussion

The soils were characterised by weak acidic to almost neutral pH values (5.3–6.8) and moisture content ranging from 16.48 % to 30.5 % in the autumn, and higher, 21.46–42.37 % in the winter (Table 1).

Table 1

Characteristics of soil in the studied localities

Selected parameters	Site I autumn	Site II autumn	Site III autumn	Site I winter	Site II winter	Site III winter
Soil pH	5.49 5.34 ± 5.71	6.04 5.87 ± 6.27	5.37 5.16 ± 5.65	6.66 6.49 ± 6.8	5.94 5.93 ± 5.95	5.3 5.16 ± 5.44
Dampness of soil [%]	17.17 16.48 ± 18.11	25.56 24.17 ± 27.32	29.53 28.85 ± 30.55	24.68 21.46 ± 27.19	29.7 28.96 ± 30.42	37.59 32.8 ± 42.37

Locality I – meadow 200 m away from the road.
Locality II – meadow 2 m away from the road.
Locality III – meadow 100 m away from the road.

Pedofauna population at the test sites varied in the period of investigations, it was significantly higher in the winter season. The highest value of 21216 specimen per square meter was noted at Site III, about 200 m away from the road, in the winter. The lowest density of 10176 specimen per square meter was found in the meadow 200 m away from the road in the autumn, where the moisture content was at its lowest (Table 1, Fig. 1).

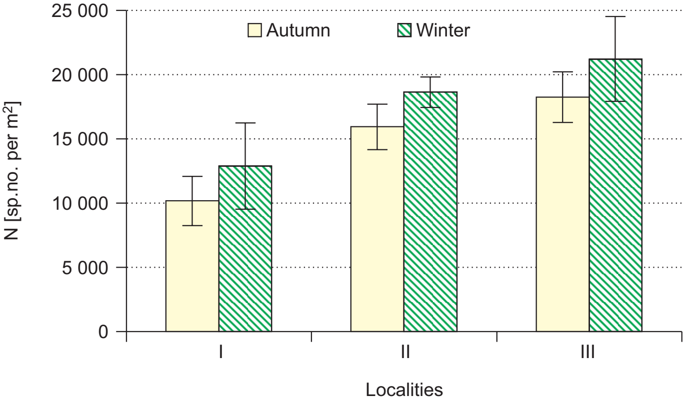

Fig. 1. Density of the soil fauna in the studied localities

The assessment of the level of pollution by Cu, Cd, Zn, Ni and Pb in the investigated meadow soils was carried out by the use of limit values for the heavy metal content set out in the Minister of Environment Regulation on the soil quality and farmland quality standards (Polish Journal of Laws Dz.U. 2002 No. 165, item 1359 of 4 October 2002). No cases of exceeding the limit values for metals were found for Group B soils (a group covering the land rated as farmland excluding the land under ponds and the land under ditches, the woodland and tree- and bush-covered land, wasteland, as well as built-up and urban areas, excluding industrial areas, mine lands and transport areas). In the investigated soils, these elements occurred in the amounts defined as permissible for this soil group [5] (Table 2).

Table 2

Content of heavy metals in meadow soils in the autumn and winter [mg · kg^{-1}]

Metal [mg/kg]		Site I autumn	Site II autumn	Site III autumn	Site I winter	Site II winter	Site III winter	The limit values*
Cu	mean range	9.88 9.54 ± 10.2	6.53 6.39 ± 6.59	11.43 10.3 ± 12.3	10.43 9.24 ± 11.8	11.3 9.92 ± 12.3	10.27 8.58 ± 13.2	150
Pb	mean range	18.81 18.2 ± 19.79	18.41 16.35 ± 20.0	40.13 38.35 ± 41.7	16.43 13.72 ± 18.3	18.62 18.08 ± 22.0	45.62 44.12 ± 47.4	100
Zn	mean range	27.97 24.39 ± 30.5	29.43 27.7 ± 30.96	30.45 27.32 ± 33.6	33.58 31.45 ± 37.9	33.51 33.61 ± 36.5	42.91 41.7 ± 44.58	300
Cd	mean range	0.69 0.55 ± 0.79	0.62 0.36 ± 0.8	0.69 0.63 ± 0.82	0.8 0.63 ± 0.93	0.6 0.52 ± 0.73	0.88 0.79 ± 0.89	4
Ni	mean range	13.72 12.86 ± 14.4	10.02 9.59 ± 10.18	8.04 8.88 ± 10.86	14.52 11.91 ± 18.4	15.29 12.33 ± 16.6	9.58 8.32 ± 15.29	100

* The limit values for the heavy metal content set out in the Minister of Environment Regulation on the soil quality and farmland quality standards for Group B soils (Polish Journal of Laws Dz.U. 2002 No. 165, item 1359 of 4 October 2002).

Cadmium is relatively easily taken up by plants, generally proportionally to its concentration in the environment. The concentration of cadmium at the test sites ranged between 0.36 to 0.93 mg per kg of dry matter and stayed within the range specified for the soil in its natural state (degree 0) according to Kabaty-Pendias [6] (Fig. 2).

There was no statistically significant correlation found between the season and the Cd content in the soil (F = 1.32; p = 0.29).

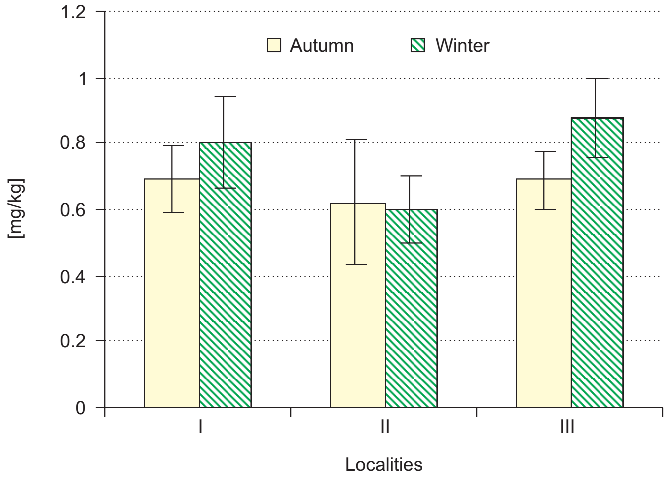

Fig. 2. The concentration of cadmium at the test sites

However, statistically significant differences were found between the content of other metals in the soil at the test site in the autumn and winter season (Table 3).

Table 3

Comparison of metal content in soil in autumn and winter – ANOVA test results

	Cu	Pb	Zn	Cd	Ni
F	14.39	11.42	71.47	1.32	6.96
p	0.0002	0.0006	0.0000	0.29	0.006

The concentration of Zn rises in the areas of increased industrial dust deposition, in the areas of intensive agricultural production and in the period of wearing out of automobile tyres. The studies carried out showed the zinc content at the level of 27.97 to 30.45 mg per kg of dry matter in the autumn. Higher levels of this element occurred in the winter at all test sites (Fig. 3).

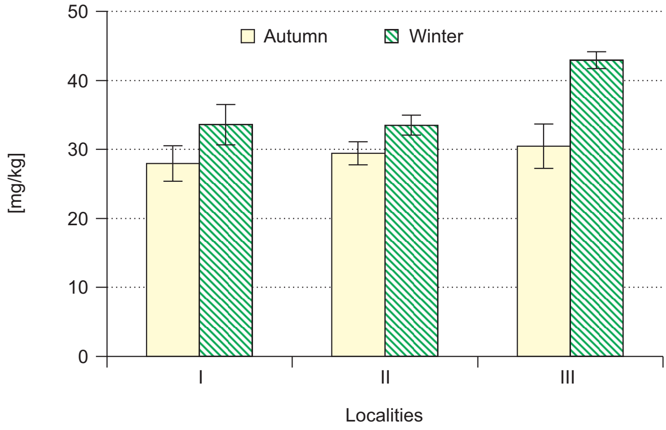

Fig. 3. The concentration of zinc at the test sites

Substantially lower Zn contents in the vicinity of the test sites (Bochnia and its surroundings), on average 7.2 mg per kg, were found by Zychowski [7]. It results from the studies that the highest Zn content in the soil occurs right next to the roadway. Some authors think that an increased Zn content occurs even 100 m from the roadway edge. It depends on the wind direction and on the traffic flow [8, 9]. This has been confirmed by the results of the present work, the highest Zn level of 42.91 mg per kg of dry matter was noted at the distance of 100 m from the road in the winter season (Site III).

The content of Cu in the studied soils ranged from 6.53 mg per kg of dry matter to 11.43 mg per kg of dry matter (Fig. 4).

The source of the soil pollution by Cu are, above all, plant pesticides, mineral fertilizers, and the application of organic wastes as fertilizers. Statistical analysis showed that the season affects the content of this element in the soil (Table 3).

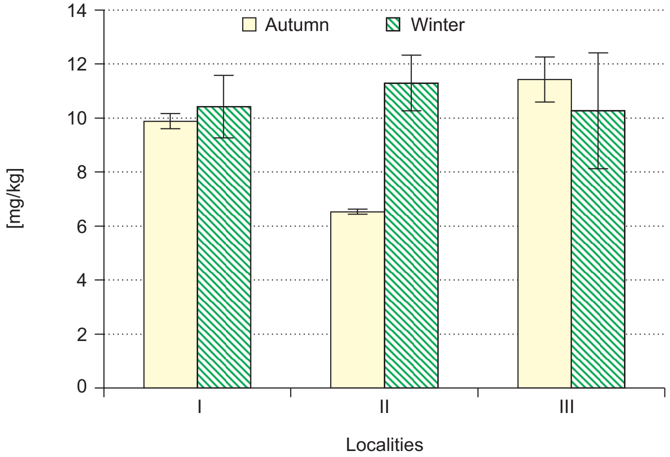

Fig. 4. The concentration of copper at the test sites

Significant differences were demonstrated in the Cu content at Site II, as well as between Cu content at Site II in the autumn, where its level was the lowest, and its content at the other sites both in the autumn (I/II p = 0.007, II/III p = 0.0002), and in the winter (p = 0.002).

Lead and all its compounds are strong poisons, harmful to humans. The source of lead pollution of the soil are motorization, non-ferrous metal industry and the sewage sludge used for soil fertilization. Pb and Cd are accumulated in the upper soil horizons. Pb concentrations indicate a significant enrichment in surface horizons from various soils in areas which receive significant acid atmospheric pollution [10]. The content of Pb at the test sites ranged between 18.41 and 45.62 mg per kg, moreover, at Site III it was over twice as high as at the other sites, both in the autumn and in the winter (Fig. 5).

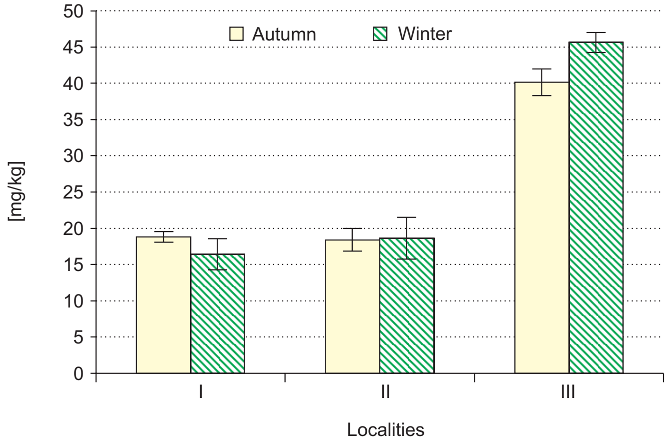

Fig. 5. The concentration of lead at the test sites

It might be associated with the position of this meadow below the road and the farmland, where from the sediments were flowing down. Significant differences were found between the Pb level at the test sites in the analysed seasons. The highest differences between the content of this metal occurred between Site III and the other meadows both in the autumn and in the winter (Table 4).

Table 4

Level of significance of differences calculated in the Tukey HSD test between studied localities

Sites	Site I autumn	Site II autumn	Site III autumn	Site I winter	Site II winter	Site III winter
Site I autumn		0.999317	0,000157	0.362651	0.997005	0.000157
Site II autumn	0.999317		0.000157	0.552970	0.963602	0.000157
Site III autumn	0.000157	0.000157		0.000157	0.000157	0.002210
Site I winter	0.362651	0.552970	0.000157		0.177510	0.000157
Site II winter	0.997005	0.963602	0.000157	0.177510		0.000157
Site III winter	0.000157	0.000157	0.002210	0.000157	0.000157	

Similarly, differences in the nickel content at the sites occurred between autumn and winter. The Ni level in the studied soil samples varied in the range from 8.04 to 15.29 mg per kg. In the winter season it was slightly higher than in the autumn, the highest at Site II situated closest to the roadway (Fig. 6).

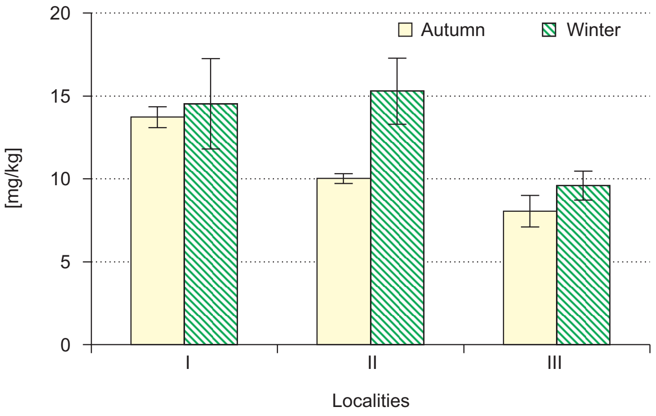

Fig. 6. The concentration of nickel at the test sites

The occurrence of nickel in the soil is determined by its presence in the parent rock, as well as the pollution, particularly with sludge sediments. Significant differences were found in the Ni content at Sites I and III in the autumn and in the winter, as well as between the seasons at the sites (I winter/ II autumn, I winter/ III autumn, II autumn/ II winter, III autumn/ II winter) (Table 5).

Table 5

Nickel of significance of differences calculated in the Tukey HSD test between studied localities

Sites	Site I autumn	Site II autumn	Site III autumn	Site I winter	Site II winter	Site III winter
Site I autumn		0.026807	0.009039	0.973872	0.683192	0.011498
Site II autumn	0.026807		0.994464	0.005760	0.001308	0.998302
Site III autumn	0.009039	0.994464		0.001967	0.000522	0.999997
Site I winter	0.973872	0.005760	0.001967		0.974922	0.002480
Site II winter	0.683192	0.001308	0.000522	0.974922		0.000626
Site III winter	0.011498	0.998302	0.999997	0.002480	0.000626	

However, despite the shown differences in Pb, Ni, Zn and Cu contents of the soil in the autumn and the winter seasons, no effect was found on the population of the soil fauna inhabiting it ($p < 0.05$).

Conclusions

1. No cases of exceeding the limit values for metals – Cd, Pb, Ni, Cu and Zn were found for Group B soils (a group covering the land rated as farmland excluding the land under ponds and the land under ditches, the woodland and tree- and bush-covered land, wasteland, as well as built-up and urban areas, excluding industrial areas, mine lands and transport areas) set out in the Minister of Environment Regulation on the soil quality and farmland quality standards (Polish Journal of Laws Dz.U. 2002 No. 165, item 1359 of 4 October 2002).
2. Statistically significant correlations were found between the Pb, Ni, Cu and Zn contents of the soil in the autumn and winter seasons at the individual sites. Higher levels occurred in the winter.
3. Such a correlation was not demonstrated for cadmium, the level of which in the soil was similar regardless of the season.
4. Despite differences in the content of the studied metals in meadow soils in the autumn and winter seasons, no effect was found on the population of the soil fauna inhabiting it.
5. Higher soil fauna density was noted in the winter season, when the moisture content of the soil was higher.

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ZAWARTOŚĆ METALI CIĘŻKICH W GLEBACH ŁĄKOWYCH W RÓŻNYCH PORACH ROKU

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Abstrakt: Badano zawartość Cd, Pb, Zn, Cu i Ni w glebach łąkowych w powiecie bocheńskim w sezonie jesiennym i zimowym 2010/2011. Łąki usytuowane były w różnej odległości od drogi: 2, 100 i 200 m. Gleby na badanych stanowiskach wykazywały odczyn od średnio kwaśnego do prawie obojętnego i wilgotność jesienią 17.17–29.53 %, natomiast w zimie 24.68–37.59 %. Wykazano istotne statystycznie różnice w zawartości Zn, Cu, Ni, Pb na poszczególnych stanowiskach w badanych sezonach. W stosunku do kadmu nie wykazano takich zależności. Pierwiastek ten w podobnym stężeniu (0.6; 0.88 ppm) występował na wszystkich stanowiskach bez względu na porę roku. Analizowano również liczebność i różnorodność pedofauny, która była większa w sezonie zimowym w glebach badanych łąk. Stwierdzono jednak, że znaczne różnice w zawartości metali nie miały wpływu na liczebność fauny glebowej na poszczególnych stanowiskach w badanych porach roku.

Słowa kluczowe: metale ciężkie, gleby łąkowe, pedofauna, zagęszczenie, różnorodność

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CHEMICAL AND BIOLOGICAL PROPERTIES OF COMPOSTS PRODUCED FROM MUNICIPAL SEWAGE SLUDGE WITH SAWDUST SUPPLEMENT

CHEMICZNE I BIOLOGICZNE WŁAŚCIWOŚCI KOMPOSTÓW WYTWORZONYCH Z KOMUNALNYCH OSADÓW ŚCIEKOWYCH Z DODATKIEM TROCIN

Abstract: The paper presents results of investigations on composting municipal sewage sludge with an admixture of sawdust. The composting was conducted in the area of sewage treatment plant for 23 weeks by means of prism method. The prisms were formed and aerated using a loader and farmyard manure spreader. Four prisms were prepared, each composed of mixtures with various volumetric proportion of components. The control object was made up entirely of sewage sludge, whereas the other prisms were formed of the sewage sludge with a 10 %, 30 % and 50 % proportion of sawdust. In order to assess the quality of obtained composts their basic chemical parameters were determined and seed germination tests were conducted.

On the basis of conducted investigations it was established among others, that with growing sawdust share in the compost mass, in relation to the sewage sludge, organic C content was increasing visibly (217.0 g $\cdot$ kg^{-1} d.m. in the compost produced of sewage sludge and 250.1 g $\cdot$ kg^{-1} d.m. in the compost with a 50 % sawdust share), whereas the quantity of basic nutrients was decreasing in the final product. All produced composts revealed low heavy metal contents, concerning this type of material. Determined contents of Cd, Cr, Hg, Ni and Pb were visibly lower than permissible in organic and organic-mineral fertilizers. Composts with the highest share of sawdust proved the best substratum for the test plant germination. Out of the test seeds sown on it, 90 % germinated, whereas only 60 % germinated when the substratum was formed solely of sewage sludge.

Keywords: sewage sludge, sawdust, compost, heavy metals

In compliance with the law in force in Poland, municipal sewage sludge is counted among wastes which may be utilized in various ways. Currently one of quite frequently used methods is its application for fertilizer purposes [1, 2]. However, it should be remembered that the priority at such materials utilization is always their use in a way

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which will not cause any negative effect on people or the environment. Information gathered by GUS (Polish *Central Statistical Office*) [3] reveals that the amount of produced municipal sewage sludge has been increasing yearly by about 5 %, so sewage treatment plants produced 359.8 thousand Mg in 2000, 486.1 thousand Mg in 2005 and 567.3 thousand Mg d.m. of sludge in 2008. The tendency, according to the estimates of the Ministry of the Environment will persist in the subsequent years, which poses serious challenge of rational management of such huge mass of sludge.

Despite the possible occurrence of certain faults, posing a potential hazard to the environment, *ie* considerable amounts of heavy metals, toxic organic compounds or presence of pathogenic microorganisms [5–7], municipal sewage sludge is more and more often used in agriculture owing to its considerable quantities of organic matter and many nutrients [5, 7, 8]. In 2008 112.0 thousand Mg d.m. of sewage sludge was managed in this way, whereas 3 years previously only half of this amount was utilised in agriculture [3]. On of the basic requirements for environmental utilization of sewage sludge is its stabilization. Unfortunately, because no parameters which stabilized sewage sludge should reveal were stated in the legal regulations, very often sludge susceptible for putrefaction is supplied to the soil, which in result produces an arduous odour causing protest of the local residents against its use in this way. Therefore, in order to avoid the above-mentioned problems the sludge producer should make every effort to prepare the sludge in an appropriate way.

One of the methods enabling proper transformation of sewage sludge prior to their application to the soil is its composting, the main objective of which is obtaining material with the properties of organic fertilizer. Properly conducted composting process allows to stabilize the sludge, destroy pathogenic organisms and decrease its mass and volume [9]. Despite many analyses of composting, this issue still requires further research. A considerable non-uniformity of physicochemical parameters of sewage sludge and local specificity of each sewage treatment plant cause that it is impossible to develop a universal composting method for this type of materials. Therefore, aiming at correct mastering of composting technology, one should consider each treatment plant individually.

The research was conducted to determine the properties of composts manufactured from sewage sludge with a supplement of sawdust and an assessment of their phytotoxicity.

Materials and methods

The research was conducted at the central sewage treatment plant owned by Water Supply and Sewerage Company in Krzeszowice. Composts were produced from municipal sewage forming in the treatment plant area and sawdust. Decision about sawdust application was affected in the first place by financial and organizational reasons of possible future enterprise involving sewage processing for compost. After analysing local potential of obtaining various structure forming materials it turned out that in the closest neighbourhood of the treatment plant sawdust is the cheapest and best structure forming material available in large quantities.

Sewage sludge and sawdust were brought to a yard and used to prepare four compost prisms of the 2.5 m base and 1.5 m high each. Each of them was composed of mixtures with various volumetric share of the following components: sewage sludge 100 % without sawdust supplement (Compost 0 % – control), sewage sludge 90 % + sawdust 10 % (Compost 10 %), sewage sludge 70 % + sawdust 30 % (Compost 30 %) and sewage sludge 50 % + sawdust 50 % (Compost 50 %). Compost mass mixing and prism forming were done by means of farmyard manure spreader and loader. During composting, which was conducted for 23 weeks, the moisture and temperature of the prisms were controlled and on this basis eventual aeration of the compost mass was determined. All in all the prisms were forked six times.

After the experiment completion compost samples were collected and subjected to the following analyses: dry mass determination – by gravimetric method at 105 °C; organic carbon (C_{org}) using oxidation-titrating with potassium dichromate(VI) in acid environment; total nitrogen – with Kjeldahl's method at Kjeltec 2300 apparatus. In order to assess individual mineral components dried composts samples were incinerated in a muffle furnace at 450 ^{o}C for 12 hours. Subsequently the remains were digested in a mixture of concentrated nitric (HNO_3) and perchloric ($HClO_4$) acids (3:2, v/v). After total acid evaporation, 20 % HCl was added to the little steamer and the sample was heated on a water bath under cover for one hour. The whole was filtered into measuring flasks – 50 cm^3 in volume. In the filtrates prepared in this way the contents of Ca, K and Na were assessed by *flame emission* method and Mg by absorption method on *atomic absorption spectrophotometer* Solaar (Thermo) and P, Cd, Cr, Cu, Ni, Pb and Zn using ICP-AES method on JY 238 Ultrace apparatus (Jobin-Yvon). Hg concentrations in filtrates were determined by AAS using an automatic mercury analyser AMA 254.

Obtained composts were also subjected to germination ability test. This experiment was conducted in 3 replications in plastic containers, 18 cm in diameter filled with 1 kg of compost. 100 seeds of cress or mustard were sown to each container. After 7 days, during which constant moisture of the material was maintained, the number of germinated seeds was counted in all containers.

Results and discussion

The wastes used for the experiment were characterized by various chemical composition (Table 1).

Sewage sludge in comparison with sawdust, as a rule revealed a higher content of minerals in conversion to dry mass of materials. Macroelement contents in sewage sludge frequently exceeded their amounts in sawdust several times, whereas microelement contents were over 50-fold higher. The highest divergence was assessed for copper, whose concentration was as much as 45-fold higher in sewage sludge than in sawdust. On the other hand, C_{org} content in sawdust was definitely higher than in sewage sludge. It is also worth mentioning than heavy metal contents in the composted sewage sludge did not exceed their maximum permissible amounts stated in Polish legislation for this type of wastes used in agriculture [2].

Table 1

Chosen properties of sewage sludge and sawdust used in experiment

Property	Unit	Sludge	Sawdust
Reaction	pH	7.80	—
Dry matter	[g · kg^{-1}]	369.2	590.0
C_{org}	[g · kg^{-1} d.m.]	256.1	489.3
N_{tot}		18.7	3.1
C : N	[-]	13.7	157.6
P	[g · kg^{-1} d.m.]	7.4	0.9
K		1.6	1.4
Ca		29.1	2.7
Mg		2.7	0.8
Na		0.5	0.6
Cd	[mg · kg^{-1} d.m.]	2.93	0.15
Cr		25.1	0.92
Cu		99.6	2.23
Hg		0.40	0.09
Ni		16.8	1.38
Pb		64.8	2.46
Zn		956.3	26.1

The differences in temperature in prisms between individual mixtures measured during the composting were relatively small (except the object with sewage sludge without sawdust, where the temperature was only slightly different from the ambient temperature). However, it is worth mentioning that most frequently the temperature of mixture with 50 % sawdust admixture was several degrees higher in comparison with the other mixtures, particularly at the initial stage of composting. At the initial stage of the experiment the temperature of prisms approximated 55 ^{o}C and then declined systematically with time reaching a value oscillating around 35 ^{o}C in the 23rd week.

Due to disadvantageous physical and chemical properties of sewage sludge, a supplement of other organic wastes is usually added to them to ensure the optimal conditions of composting. This measure ensures among others a suitable aeration of compost mass or C : N ratio (20–30 recommended at the initial phase) [10], which is crucial in the process of organic matter decomposition and enzymatic activity [11]. Recommended initial C : N quantitative ratio was maintained only in case of two mixtures with the highest proportion of sawdust. Initially its value in the prepared compost materials was as follows: compost – 0 % sawdust 13.7; compost – 10 % sawdust 16.1; compost – 30 % sawdust 21.0 and compost – 50 % sawdust 23.2. However, beside the composting conditions, compost fertilizer value is mainly affected by the kind of applied wastes and their share in individual mixtures [12].

Properties of products obtained in result of six month composting of sewage sludge and its mixtures with sawdust were presented in Table 2. Their pH was neutral, pH value of three composts with sawdust admixture was on an approximate level, oscillating around pH = 7.5, whereas in case of sewage sludge composts was higher by almost a unit.

Changeability of organic carbon content between analyzed composts was considerable and ranged from 198.1 g · kg^{-1} d.m. to 250.1 g · kg^{-1} d.m. A comparison of the obtained results with the amount of C_{org} in the initial components (Tables 1 and 2) shows an obvious diminishing of its content in result of composting. Also other authors reported carbon loss during composting [13, 14]. This element content in composts was strictly positively correlated with its amount in the initial material. However, it is worth mentioning that the lowest contents of C_{org} were assessed in compost with a 10 % sawdust supplement. It may be explained by the fact that a relatively small admixture of sawdust to sludge on one hand caused an increase in C in the compost mass, on the other, through loosening the structure it contributed to activating organic matter breakdown process leading to greater carbon losses. In the other composts with 30 and 50 % sawdust supplements, the amounts of C_{org} introduced to the compost mass were big enough, so that despite less intensive breakdown of organic matter, C_{org} content was bigger in comparison with the compost manufactured solely of sewage sludge (Table 2).

Table 2

Selected properties of composts produced from municipal sewage sludge with sawdust supplement (23 weeks of composting)

Property	Unit	Compost 0 %*	Compost 10 %	Compost 30 %	Compost 50 %
Reaction	pH	8.36	7.51	7.50	7.42
Dry matter	[g · kg^{-1}]	395.6	521.3	510.6	462.3
C_{org}	[g · kg^{-1} d.m.]	217.0	198.1	232.3	250.1
N_{tot}		16.7	15.5	15.6	15.1
C : N	[-]	13.0	12.8	14.9	16.5
P	[g · kg^{-1} d.m.]	6.9	6.6	6.5	6.7
K		1.6	1.8	1.8	1.6
Ca		28.2	28.0	27.2	26.5
Mg		2.6	2.7	2.6	2.5
Na		0.6	0.7	0.9	0.8
Cd	[mg · kg^{-1} d.m.]	2.91	2.93	2.87	2.71
Cr		26.0	25.6	24.4	22.4
Cu		99.6	93.2	86.8	81.9
Hg		0.42	0.40	0.40	0.38
Ni		19.6	18.2	16.4	16.4
Pb		76.4	79.2	82.4	79.3
Zn		1149.5	962.2	913.9	852.7

* Sawdust share in compost mixture (v/v).

Because of definitely lower content of nitrogen in sawdust in relation to its amount in sewage sludge, the highest content of this element was assessed in compost produced of sewage sludge without supplement, whereas the lowest in a mixture with the highest share of sawdust (Table 2). Also nitrogen transformations occurring during composting led to diminishing of its content in all obtained products. This element content in compost of sewage sludge was lower by *ca* 11 % in comparison with the initial material (Tables 1 and 2).

The outcome of diversified contents of carbon and nitrogen in the analysed composts was the value of C : N ratio. Its value 10–15 is treated as an indicator of compost maturity [15]. A comparison of previously stated values of this index, assessed in freshly prepared compost mixtures with the results obtained after composting completion (Table 2) reveals that the higher its value at the beginning of the process the higher was its decline. Relatively high values of C : N ratio in composts with 30 % and 50 % share of sawdust may testify their not full maturity.

Differences in the content of the other macroelements (P, K, Ca, Mg, Na) between individual composts were relatively small (Table 2). Very often quantities of these elements in the final products were decreasing with increasing sawdust share in the compost mass. Phosphorus content in the composts on the level of *ca* 7 $gP \cdot kg^{-1}$ d.m. was rather average considering the compost produced of sewage sludge, but clearly bigger than the minimum amount (2 $gP_2O_5 \cdot kg^{-1}$ d.m.) as required by the Regulation of the *Ministry of Agriculture and Rural Development* (MARD) of 18 June 2008 [16] for solid organic fertilizers in which phosphorus content is declared. As results from other authors' investigations [8, 15], sewage sludge generally contains small amounts of potassium. The fact was confirmed in the presented investigations because potassium quantities assessed in the composts were only between 1.6 and 1.8 $gK \cdot kg^{-1}$ d.m.

One of crucial parameters of compost fertilizer value is heavy metal content. Analysis of heavy metal contents in the obtained composts showed their highest amounts in the compost obtained of sewage sludge, whereas the lowest in compost with the highest sawdust supplement (Table 2). Obtained results are on one hand the outcome of increasing mineral content in result of organic compound mineralisation occurring during composting process [14], and on the other are due to dilution obtained through an addition of sawdust containing small amounts of metals. All heavy metal contents (Cd, Cr, Hg, Ni and Pb) in the analysed materials (Table 2), as required by the MARD Regulation [16], were visibly smaller than the values permissible in organic and organic-mineral fertilizers.

Germination tests of cress (*Lepidium sativum* L.) and mustard (*Sinapis alba* L.) were conducted to determine phytotoxicity of the composts. The tests revealed that the best substratum was compost produced of sewage sludge with a 50 % sawdust supplement. On this substratum 86 and 92 out of 100 seeds respectively of cress and mustard germinated (Table 3).

Table 3

Results of germination test of cress and mustard seeds on composts produced from municipal sewage sludge with sawdust admixture

Material	Number of sown seeds	Number of germinated seeds	
		crees	mustard
Compost 0 %*	100	56	57
Compost 10 %	100	78	80
Compost 30 %	100	90	78
Compost 50 %	100	86	92
Control	100	89	94

* Sawdust share in compost mixture (v/v).

The plants germinated slightly more weakly on the compost with 30 % sawdust addition. The compost obtained from the sewage sludge without any admixture proved the most toxic because only about 60 % of the seeds of both plants sown on it germinated.

Conclusions

1. Composts produced of municipal sewage sludge and sawdust may be a valuable organic fertilizer because in view of its chemical composition it meets all the requirements posed for the fertilizers of this type. It is abundant in essential fertilizer components (organic matter, N and P) and does not contain excessive amounts of heavy metals.
2. Sawdust supplement to sewage sludge in the amount higher than 30 % of sewage volume contributed to increase in the content of organic carbon and decrease in heavy metal concentrations in the composts obtained from mixtures of this type.
3. Composts originating from sewage sludge and sawdust were characterised by a higher biological value in comparison with the composts produced solely from sewage sludge.

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CHEMICZNE I BIOLOGICZNE WŁAŚCIWOŚCI KOMPOSTÓW WYTWORZONYCH Z KOMUNALNYCH OSADÓW ŚCIEKOWYCH Z DODATKIEM TROCIN

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Abstrakt: W pracy przedstawiono wyniki badań dotyczące kompostowania komunalnych osadów ściekowych z dodatkiem trocin. Kompostowanie prowadzono na terenie oczyszczalni ścieków, metodą pryzmową przez 23 tygodnie. Do formowania oraz napowietrzania pryzm użyto ładowarkę i rozrzutnik obornika. Przygotowano 4 pryzmy, a każda z nich składała się z mieszanin o różnym udziale objętościowym komponentów. Obiekt kontrolny składał się wyłącznie z osadu ściekowego, natomiast pozostałe pryzmy formowano z osadu ściekowego z 10 %, 30 % oraz 50 % udziałem trocin.

W celu oceny jakości otrzymanych kompostów badano ich podstawowe parametry chemiczne oraz przeprowadzono testy kiełkowania nasion. Na podstawie przeprowadzonych badań stwierdzono m.in., że wraz ze wzrostem udziału trocin w masie kompostowej, w stosunku do osadów ściekowych, wyraźnie zwiększała się zawartość węgla organicznego, natomiast zmniejszała się ilość podstawowych składników pokarmowych w produkcie końcowym. Wszystkie wytworzone komposty charakteryzowały się niską, jak na tego typu materiał, zawartością metali ciężkich. Komposty z największym udziałem trocin okazały się najlepszym podłożem do kiełkowania roślin testowych.

Słowa kluczowe: osad ściekowy, trociny, kompost, metale ciężkie

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Małgorzata NABRDALIK[1]

DISINFECTIVE ACTIVITY OF 8-HYDROXYQUINOLINE SULFATE ON MOULDS

AKTYWNOŚĆ DEZYNFEKCYJNA SIARCZANU 8-HYDROKSYCHINOLINY WZGLĘDEM GRZYBÓW PLEŚNIOWYCH

Abstract: The aim of conducted research was the estimation of 8-hydroxyquinoline sulfate activity on selected mould strains isolated from the buildings with biodeterioration evidence. In the tests for the fungicidal activity, 6 working concentrations rangeing from 0.01 % to 1.0 % of 8-hydroxyquinoline sulfate were tested in terms of their efficiency. All strains under study were isolated from the building compartments and they were: *Cladosporium cladosporioides, Alternaria tenuissima, Stachybotrys chartarum, Aspergillus flavus* and *Penicillium notatum.* The effect of fungicide activity against moulds was assessed by means of diffusion cylinder-plate method. The rate of mycelial growth and the ability to germinate in the presence of the tested chemical was also estimated. In the cylinder-plate method the criterion for assessing fungicidal activity was based on the size of the zone of growth inhibition (measured in mm). The biggest – 85.0 mm zone of growth inhibition was obtained at the concentration of 1.0 % for *Aspergillus* and additionally for *Penicillium* at the concentration of 0.75 %. The same sizes of the zones (85.0 mm) were noted for *Stachybotrys* at 0.5 % concentration, and for *Cladosporium* and *Alternatia* at 0.25 % concentration. The increase in concentrations in all cases did not have an effect on the size of the zones of growth inhibition. On the basis of the growth rate of mycelium, it was noted that the most sensitive to 8-hydroxyquinoline sulfate activity are *Stachybotrys* and *Alternaria* strains. The lowest inhibitory dose which inhibited the mycelial growth completely was 0.2 %. The effective activity of the examined chemical at following concentrations: 0.25; 0.5; 0.75; and 1 % against the ability to germinate was observed for *Cladosporium*, *Stachybotrys* and *Alternaria.* The results obtained in the research showed that the inhibition of mycelium and spores were effective in case of 1 % of 8-hydroxyquinoline sulfate.

Keywords: 8-hydroxyquinoline sulfate, moulds, disinfection

Filamentous fungi, commonly called moulds, when growing in buildings may cause biological corrosion and pose health hazard to people in the buildings. Biological corrosion of building materials, occuring due to very intensive surface development of moulds can worsen the aesthetic values of the building and may cause the loss of mechanical properties of infested elements [1]. However, much worse than corrosion of materials is the influence of moulds on peoples' health. They have been reported [2–4]

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many times to be the reason for many diseases. Some of the moulds are allergic for people with a healthy immune system. However, they may damage the neural system, liver, kidneys or cause changes leading to cancer diseases of people with immune deficiency. Besides, moulds have specific biological properties and biochemical abilities enabling them to produce many toxic metabolites, including the most dangerous ones – mycotoxins (aflatoxin, ochratoxin) [5, 6].

The basic method used when fighting against moulds on building materials is introducing chemicals with biocidal properties (fungicides), into materials during the production process or during the usage.

The efficacy of chemical methods for the protection of building materials against moulds depends on fungicidal activity of applied chemical and the type of the moulds. Therefore, tested moulds should be representative for the environment, in which disinfection will be carried out. It cannot be one dominant species but the mixture of several strains, as in natural environment we deal with mixed mycoflora.

The aim of the research was the estimation of fungicidal activity of 8-hydroxyquinoline sulfate with reference to typical mycoflora occuring in buildings with biodeterioration evidence. The assay of moulds sensitivity was run in relation to mycelium and spores. Obtained reults were used to analyse the abilities to apply the most effective concentrations of the chemical.

Materials and methods

Moulds under study belonged to most frequently isolated moulds from buildings with biodeterioration evidence [7], and based on performed identification they were categorized as:

- *Alternaria tenuissima* (Fries) Wiltshire,
- *Aspergillus flavus* Link,
- *Cladosporium cladosporioides* (Fresenius) de Vries,
- *Penicillium notatum* Westling,
- *Stachybotrys chartarum* (Ehrenberg ex Link) Huges.

The strains were kept on agar slant tubes containing 10 cm^3 of Sabourauda medium. They were incubated at 25 ^oC for 14 days. After this period, the sporulating mycelium was washed three times with the isotonic solution of sodium chloride. The density of material, measured with a counting chamber Thoma type, was stable and equal to $1 \cdot 10^6$ cells/1 cm^3.

For further studies the suspension of particular moulds species was used as well as the mixture of the moulds spores in proportion (1 : 1 : 1 : 1 : 1).

In the tests for fungicidal activity, the efficacy of 8-hydroxyquinoline sulfate was tested in 6 working concentrations of: 0.01 %, 0.1 %, 0.25 %, 0.5 %, 0.75 % and 1.0 %.

The fungicidal activity of 8-hydroxyquinoline sulfate was assessed on the basis of:

- the cylinder-plate diffusion method,
- the intensity of mycelial growth rate,
- the ability of spores to germinate.

Fungicidal activity of the chemical applied was assessed with the modified cylinder-plate diffiusion method where 3 sterile glass cylinders of 10 mm diameter and 12 mm of height were placed on Petri dishes (∅ 100 mm). Next, the dishes were poured with 20 cm^3 of Sabourauda medium inoculated with particular moulds species and the mixture of the spores of the tested moulds (of $1 \cdot 10^6$ cell/cm^3). During the medium inoculation its temperature did not exceed 50 °C. The plates with agar were then left at room temperature to solidify. After removing the cylinders, the wells were filled with 0.2 cm^3 of the tested chemical in respective concentrations. The control treatment was the wells filled with sterile water. The tests were conducted in six replicates (A, B, C, D, E, F), where each well was a single treatment. The samples were incubated at 25 ^{o}C for 3 weeks, and the measurements were taken after 3, 7, 10, 14 and 21 days. The disinfective efficacy of the tested chemical was assessed on the basis of the growth inhibition zones measurement made exact to 0.1 mm. In replicates, where moulds overgrew the medium around the wells completely, the value of the measurement was assumed 10 mm. In cases when the mycelium growth was not noted the measurement value was assumed 85 mm.

The indication of fungicidal activity based on the intensity of mycelial growth rate was conducted on Sabourauda medium with the addition of the consecutive concentrations of the chemical. Agar discs of 10 mm diameter overgrown with 2-week mycelium of tested moulds were placed on the medium on Petri dishes.

The control treatment was prepared on a Petri dish with Sabourauda medium (without the chemical) and mycelium disc. The diameter of mould colonies was measured every 3 days exact to 0.1 mm, from the beginning of the mycelial growth recorded in the control dishes. The measurements were recorded until the mould in the control treatment reached the edge of the dish. The test was conducted in four replicates (A, B, C, D), while one Petri dish with the mycelial disc represented a single replica. The samples were incubated at 25 °C.

The activity of tested chemical against the mycelial growth was assessed on the basis of the growth rate index (T), calculated with the following formula [8, 9]:

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

where: T – growth rate index,
A – the mean value of colony diameter measurement [mm],
D – the length of an experiment [days],
b_1, b_2, b_x – increase in diameter since the last measurement,
d_1, d_2, d_x – number of days passed since the last measurement.

Test results were calculated as the percentage of the growth inhibition.

Indication of fungicidal activity was also tested on the basis of the spores ability to germinate. For this purpose 0.02 cm^3 of the consecutive concetrations of 8-hydroxyquinoline sulfate were placed on the 1 cm^2 of the slide. After drying, preparations were inoculated with 0.02 cm^3 of the suspension containing spores of the tested moulds. The density of inoculum was selected in a way that in the field of vision under a medium magnification of a microscope 50–60 spores were observed. The slides with the drops of suspension were placed in moist chambers. The chambers were prepared as Petri dishes with blotting paper discs on the bottom, saturated with sterile water. The control treatment was pure spores suspension placed on a clean slide. The test was conducted in four replicates (A, B, C, D). The germination of 50 spores was assessed after 24 hours in the field of vision under a microscope. When rating germination, the scale introduced by Burgiel [8, 9] and Kowalik [10] was used:

0 – non-germinating conidia,
1 – the length of a germ tube shorter than the spore length,
2 – the length of a germ tube equal to the length of a spore,
3 – the length of a germ tube twice as long as the spore length,
4 – branching germ tube repeatedly longer than a conidium.

The influence of tested chemicals on the development of mould spores was assessed on the basis of the spores germination index, calculated with the formula:

$$I = \frac{\sum (n \cdot a) \cdot 100}{N \cdot 4}$$

where: I – spores germination index,
n – number of the spores in the specific grade on the scale,
a – grade on the scale,
N – general number of the counted spores,
4 – the highest grade of the scale.

The efficacy of the fungicide was assessed as the % of the spores development inhibition.

Results

8-hydroxyquinoline sulfate $(C_9H_7NO)_2 \cdot H_2SO_4$ is a chemical with known bactericidal and fungicidal properties, which has not been used so far against moulds growing on building materials.

Assay of biocidal activity of tested chemicals was based on the size of the growth inhibition zone, measured in mm. In case of 8-hydroxyquinoline sulfate the lowest concentration of the chemical was taken into account above which no significant differences were noted but the biggest growth inhibition zones were obtained. The biggest – 85.0 mm zones were obtained in the concentration of 1.0 % for *Aspergillu*s and the mixed treatment and additionally for *Penicillium* in the concentration of 0.75 %. The same sizes of the zones (85.0 mm) were noted for *Stachybotrys* in 0.5 % concentration, and for *Cladosporium* and *Alternaria* in 0.25 % concentration. The increase in concentrations in all cases did not have an effect on the size of the zones and the differences between them were not significant (Table 1).

Table 1

Zones of the growth inhibition of tested moulds in the presence of 8-hydroxyquinoline sulfate

Mould strain	Control	Concentration of applied chemical [%]					
		0.01	0.1	0.25	0.50	0.75	1.0
Penicillium	10.00 a	10.00 a	10.00 a	60.83 b	70.00 c	85.00 d	85.00 d
Aspergillus	10.00 a	10.00 a	10.00 a	10.00 a	10.00 a	10.00 a	85.00 b
Cladosporium	10.00 a	10.00 a	16.33 b	85.00 c	85.00 c	85.00 c	85.00 c
Stachybotrys	10.00 a	10.00 a	10.00 a	10.00 a	85.00 b	85.00 b	85.00 b
Alternaria	10.00 a	10.00 a	10.00 a	85.00 b	85.00 b	85.00 b	85.00 b
Mixed treatment	10.00 a	10.00 a	10.00 a	10.00 a	10.00 a	10.00 a	85.00 b

Lower case – significant differences ($p \leq 0.05$).

The values of inhibition zones were evaluated on the basis of obtained results and contributed to a specification of three mould groups according to their activity:

1st group – zone of the growth inhibition below 40 mm – resistant strain,
2nd group – zone of the growth inhibition 40–60 mm – medium-sensitive strain,
3rd group – zone of the growth inhibition above 60 mm – sensitive strain.

In order to obtain the value of the inhibition zone above 40 mm, for all of the strains at the same time, the 8-hydroxyquinoline sulfate should be applied in the concetration of 1.0 %. However, for *Penicillium, Cladosporium* and *Alternaria* the lowest inhibitory concentration was 0.25 % and for *Stachybotrys* 0.5 %. 8-hydroxyquinoline sulfate has a fungicidal effect against all tested mould strains and their spores mixture in the concentration of 1.0 % and the measured inhibition zones were the biggest – equal to 85.0 mm.

The activity of 8-hydroxyquinoline sulfate on the linear growth of mycelium of tested moulds was determined on the basis of the *growth rate index* (GRI). In the conducted test, the diameter of the colonies [mm] growing on the media containing consecutive concentrations of the chemical was measured including the increase in the diameter at time intervals. The objective was to find the lowest concentration for which the GRI had low values, statistically significant in respect to the control treatments.

The most sensitive to 8-hydroxyquinoline sulfate were *Stachybotrys* and *Alternaria* strains. The lowest inhibitory dose which inhibited the mycelial growth completely was 0.25 %. Slightly higher concentration – 0.5 % inhibited *Cladosporium*, and the next one – 0.75 % was the lowest inhibitory concentration to *Aspergillus*. In case of *Penicillium* and the mixed treatment, the concentration which inhibited the growth was 1 %. For all other concentrations, the growth of tested moulds was not observed above the lowest inhibitory value (GRI = 0) (Table 2). The growth of mycelium of all tested moulds was inhibited in 100 % at 1 % concentration of the sulfate (Fig. 1). Furthermore, the solutions of 8-hydroxyquinoline sulfate did not affect the morphology of the colony only brighter pigmentation of an aerial mycelium was noted. The structure of the colonies was not changed. The production of the spores was inhibited in all combinations.

Table 2

The growth rate index of tested moulds in the presence of 8-hydroxyquinoline sulfate

Mould strain	Control	Concentration of applied chemical [%]					
		0.01	0.1	0.25	0.50	0.75	1.0
Penicillium	25.35 c	23.29 c	23.87 c	23.96 c	24.29 c	20.42 b	0 a
Aspergillus	16.03 e	15.40 e	13.23 d	10.52 c	2.29 b	0 a	0 a
Cladosporium	15.60 e	14.97 d	8.31 c	5.58 b	0 a	0 a	0 a
Stachybotrys	24.37 d	22.70 c	7.23 b	0 a	0 a	0 a	0 a
Alternaria	33.05 d	32.06 c	29.97 b	0 a	0 a	0 a	0 a
Mixed treatment	25.95 e	22.37 c	24.37 d	23.20 c	22.46 c	20.42 b	0 a

Lower case – significant differences ($p \leq 0.05$).

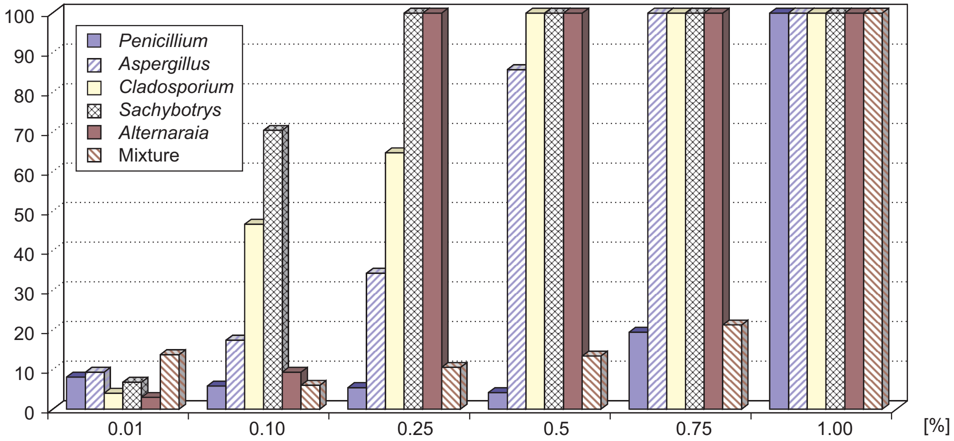

Fig. 1. The decrease in the growth rate of tested moulds after application of 8-hydroxyquinoline sulfate

In the fight against moulds the desired effect of a fungicide application is the complete inhibition of the mycelial growth, therefore the concentrations considered fungicial are only those in which 100 % of efficacy was obtained against all tested moulds and the mixture of their spores. The condition was fulfilled only by 1 % 8-hydroxyquinoline sulfate (Fig. 1). The aforementioned concentration will be treated at the same time as a minimal concentration inhibiting the development of mould mycelium.

In the laboratory research the influence of 8-hydroxyquinoline sulfate on the germination of tested mould spores was estimated. The influence of the chemical under study on the development of spores was estimated on the basis of the microscopic observations, which also enabled determination of the *germination index* (GI), taking into account the grade of the hyphae germination on the scale 0–4.

For the following moulds: *Penicillium, Cladosporium* and *Stachybotrys* the spores germination was inhibited starting from the concentration of 0.5 %. There were no significant differences between the consecutive concentrations: 0.5; 0.75 and 1 %. For *Aspergillus* only 1 % concentration inhibited effectively spores germination. The value of GI was 0 similarly to the values for *Cladosporium* and *Stachybotrys*. It was also observed that in case of *Alternaria* there were no statistically significant differences between the concentrations (from 0.1 do 1 %). The lowest value of GI was obtained when applying 1 % dose (GI = 0.66 %) (Table 3).

Table 3

The ability of the spores to germinate in the presence of 8-hydroxyquinoline sulfate

Mould strain	Control	Concentration of applied chemical [%]					
		0.01	0.1	0.25	0.5	0.75	1.0
Penicillium	24.50 e	14.33 d	7.16 c	4.50 b	1.83 a	0.66 a	0.33 a
Aspergillus	20.50 f	12.50 e	7.16 d	4.33 c	1.16 b	0.33 ab	0 a
Cladosporium	35.33 d	23.16 c	4.00 b	2.83 ab	0.83 a	0.50 a	0 a
Stachybotrys	74.50 d	32.66 c	6.16 b	4.33 ab	1.33 a	0.33 a	0 a
Alternaria	81.33 c	24.33 b	4.50 a	2.50 a	1.66 a	1.16 a	0.66 a

Lower case – significant differences ($p \leq 0.05$).

Also the highest reduction in the number of spores ranging from 97.34 to 100 % was obtained in the concentration of 1 %. (Fig. 2).

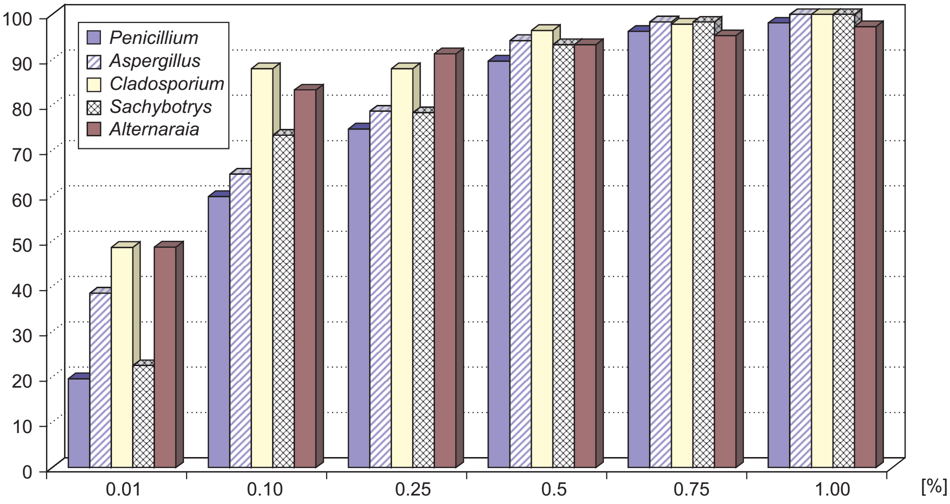

Fig. 2. The reduction of germinating spores after application of 8-hydroxyquinoline sulfate [%]

During the microscopic observation it was noted that the chemical did not affect the morphology of the spores of tested moulds. The changes in the size, colour and external structure of the spores were not observed.

When assessing the toxicity of fungicides the scale introduced by Kowalik and Krechniak [10] can be used:

0–49 % – ineffective chemical,
50–79 % – sufficiently effective chemical,
80–90 % – efficient chemical,
91–100 % – very efficient chemical.

Based on the scale, it was established, that the fungicide is biologically active if its toxicity is over 50 % [8]. However, in the presented study the concentration of the chemical was regarded as fungicidal, for which the effectiveness towards the spores was 90 %. The above assumption was true for the spores of all tested strains only in case of 8-hydroxyquinoline sulfate in the concentrations of 0.75 and 1 %.

The activity of biocidal chemicals against the microorganisms is a complex and multi-stage reaction, which mechanism has not been eventually known. Therefore, it is difficult to predict the effect on the moulds of different fungicidal environment.

The conducted research enables to state that only on the basis of obtained results concerning the growth of vegetative mycelium and the reaction of the spores towards the specific chemical, it is possible to determine its fungicidal activity. In the studies only 8-hydroxyquinoline sulfate in the concentration of 1 % was inhibitory for both the mycelium and the spores.

Summary and conclusion

The research proved a considerable diversity of sensitivity among particular mould strains to particular concentrations of 8-hydroxyquinoline sulfate included in tests and enabled to draw the following conclusions:

1. An impact of the chemical on the linear growth of mycelium can be determined on the basis of the growth inhibition zones and the growth rate index. The effective concentration of the chemical is the one which causes the inhibition zone bigger than 60 mm or inhibits the mycelium growth completely.
2. The sensitivity of the spores should be determined on the basis of a germination ability in the presence of the chemical. The effective chemical is characterized by over 90 % of efficacy.
3. The conducted tests prove that biological chemicals display a varied biocidal activity against mycelium and spores. The fungicidal effect was stronger in case of the spores rather than the mycelium. Therefore, the estimation of fungicidal activity should be conducted on the basis of sensitivity to the vegetative mycelium and mould spores.
4. On the basis of performed analysis it was stated that heterocyclical chemicals containing N display high fungicidal activity. Application of 8-hydroxyquioline sulfate inhibits the mycelial growth and the spores germination of the moulds.
5. The sensitivity of moulds to fungicide is a species trade. The most sensitive to 8-hydroxyquinoline sulfate were the following strains: *Cladosporium cladosporioides*, *Stachybotrys chartarum* and *Alternaria tenuissima*, and the most resistant strains were: *Aspergillus flavus* and *Penicillium notatum*.

6. The estimation of fungicial activity should be conducted on moulds which are representative for the environment, in which disinfection will be carried out. It should not be one dominant species, but the mixture of several strains.

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AKTYWNOŚĆ DEZYNFEKCYJNA SIARCZANU 8-HYDROKSYCHINOLINY WZGLĘDEM GRZYBÓW PLEŚNIOWYCH

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Abstrakt: W niniejszej pracy przeprowadzono badania mające na celu ocenę działania siarczanu 8-hydroksychinoliny na wybrane szczepy grzybów strzępkowych wyizolowanych z budynków z oznakami biodeterioracji pleśniowej. W testach aktywności grzybobójczej sprawdzono działanie siarczanu 8-hydroksychinoliny w 6 stężeniach roboczych od 0,01 do 1,0 %. Grzybami testowymi były gatunki wyizolowane z przegród budowlanych, a mianowicie: *Cladosporium cladosporioides*, *Alternaria tenuissima*, *Stachybotrys chartarum*, *Aspergillus flavus* oraz *Penicillium notatum*. Efekt biobójczego działania związku na grzyby pleśniowe oceniono metodą dyfuzyjną płytkowo-cylinderkową. Przeprowadzono również ocenę tempa wzrostu grzybni oraz zdolność kiełkowania zarodników grzybów pleśniowych w obecności testowanego związku. W metodzie dyfuzyjnej płytkowo-cylinderkowej podstawą do określenia aktywności biobójczej były rozmiary strefy zahamowania wzrostu [mm]. Największe – 85,0 mm strefy zahamowania wzrostu uzyskano dla stężenia 1,0 % dla *Aspergillu*s oraz dodatkowo dla *Penicillium* w stężeniu 0,75 %. Takie same wartości stref (85,0 mm) uzyskano dla *Stachybotrys* przy 0,5 % stężeniu, a dla *Cladosporium* i *Alternaria* przy 0,25 %. Wzrost o kolejne stężenia we wszystkich przypadkach nie miał wpływu na wartości stref zahamowania wzrostu. Na podstawie oceny tempa wzrostu grzybni stwierdzono, iż najbardziej wrażliwe na działanie siarczanu 8-hydroksychinoliny są szczepy *Stachybotrys* oraz *Alternaria*. Najniższa dawka hamująca całkowicie wzrost grzybni to 0,2 %. Ponadto zaobserwowano skuteczne działanie 0,25; 0,5; 0,75 i 1 % badanego związku na zdolność kiełkowania zarodników *Cladosporium, Stachybotrys* i *Alternaria*. Z przeprowadzonych badań wynika, że inhibicję zarówno w stosunku do grzybni, jak i zarodników, wykazał 1 % siarczan 8-hydroksychinoliny.

Słowa kluczowe: siarczan 8-hydroksychinoliny, pleśnie, dezynfekcja

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QUANTITATIVE ANALYSIS OF AEROBIC CULTIVABLE BACTERIA AND SOIL TOTAL ENZYMATIC ACTIVITY OF KIELCE AND RUDKI URBICENOSE

ANALIZA ILOŚCIOWA TLENOWYCH BAKTERII HODOWALNYCH ORAZ CAŁKOWITEJ AKTYWNOŚCI ENZYMATYCZNEJ GLEBY URBICENOZY KIELC I RUDEK

Abstract: The microbiological and biochemical analysis of two urban soil samples, from Swietokrzyskie province (Kielce, Rudki), were performed. The aim of this study was the quantitative analysis of aerobic bacterial microflora and determination of total enzymatic activity of soil from area with high level of street traffic (Kielce) and from former pyrite mine region (Rudki), where uranium ore were extracted. The commercial media (TSA, LB, MacConkey, M9 and King B agars) and soil extract agars were used for soil microorganisms isolation. The bacteria were cultivated in two temperatures: +25 °C and +4 °C. From Kielce urbicenose, amount of soil bacteria cultivated on commercial media were higher in case of culture in +25 °C (from 10 to 10^8 times more depending on used medium), whereas on soil extract agar almost 2 times more microorganisms were found in +4 °C. For soil contamined by uranium (Rudki), abundant bacterial growth in both temperatures were observed only on soil extract agar. The total ureolytic, proteolytic and lipolytic activities of soil samples were also defined. In case of soil sample from Kielce all from the determinated activities were found, whereas for soil from Rudki only lipolytic activity was noted.

Keywords: soil bacteria, heavy metals, total enzymatic activity.

Pollution of environment by uranium is a serious problem because this element in the oxidized U(VI) form is soluble and highly toxic [1]. Its toxicity concern not only plants

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and animals, but also bacteria [2]. However, there is known, that soil microorganisms are much more sensitive to other heavy metals. In uranium polluted environments, the relatively numerous bacterial microflora, including *Proteobacteria*, *Acidobacteria* and *Bacteroidetes*, were observed [3]. There is known, that microorganisms naturally occurring in such areas influence on migration of heavy metals, including uranium [2].

There is no papers about amount of cultivable bacterial microflora and total biochemical activity of uranium contaminated soils.

The aim of thise work was the quantitative analysis of aerobic cultivable bacterial microflora as well as determination of total enzymatic activity of soil from area with heavy traffic (Kielce) and former piryte mine region (Rudki), where uranium ore was extracted.

Materials and methods

Soil samples – samples from the surface soil layer were collected aseptically into sterile containers by triple puncture with Egner's stick, on depth 20 cm. The research material was collected on November 18th, 2010 and consist of two soil samples: the first was from degraded urban soil from Kielce (marked as G10 sample) while the second was from pyrite mine area in Rudki (marked as G12 sample) (Fig. 1).

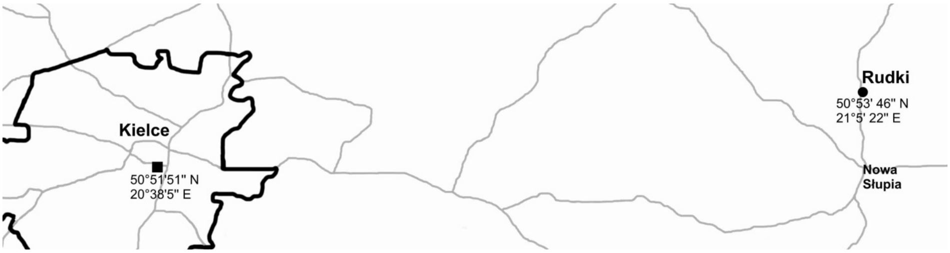

Fig. 1. Localization of the soil samples G10 (■) and G12 (●) collection

Chemical analysis of the soil samples – heavy metals content in the sample G12 were determined by ICP-MS, while in sample G10 – by FAAS method.

Soil bacteria isolation – 1 g of soil suspension (G10 or G12, respectively) in 100 cm^3 sterile Winogradsky solution was intensively stirred (20 min 500 rpm). After sedimentation of soil particles solutions were diluted up to 10^{-6} and plated on Petri dishes with media: Luria-Bertani (LB) agar, minimal M9 agar, tryptic-soy agar (TSA), King B agar, MacConkey agar and soil extract agar (SEA). Cultures were incubated at +25 °C up to 7 days and at +4 °C up to two weeks. Amount of bacteria (cfu/1g of wet soil) was determined based on the number of bacterial colonies grown on particular media.

Determination of the total biochemical activity of soil samples – ureolytic activity was determined according to Moreno et al method by detection ammonium ions in phenol-hypochloride assay [4]. Proteolytic activity of soil samples (suspension of 0.5 g soil and 0.4 cm^3 of toluene, incubated 15 min at room temperature) was determined in azocasein test. Azocasein (20 mg) suspension was incubated with soil samples (G10 or G12, respectively) by 24 h at +25 °C. One unit of proteolytic activity was defined as ability to hydrolyze 1 mg of azocasein per hour [5, 6]. Lipolytic activity was defined according to Margesin et al using *p*-nitrophenyl butyrate (pNPB) as a substrate [7].

Results and discussion

The number of soil microorganisms strictly depends on soil conditions [8]. For the cultivation of aerobic bacteria from two urban soil samples six different microbiological media were used. Those media allow for growth of microorganisms with high as well as low nutritional requirements. The amount of microorganisms cultured from soils was varied. In the case of sample G10 (Kielce), microbial growth on all media was observed, but most abundant was on soil extract agar (SEA). Amount of bacteria ranged from 10^5 to 10^9 cfu/g of soil and was higher (except for MacConkey agar) when the cultivation temperature was +25 °C. In other studies, similar amounts of microorganisms cultured from various urban soils were observed [9, 10]. A completely different situation was observed for the G12 sample (Rudki). In this case, bacteria were grown only on SEA medium (at both temperatures) and on King B agar (only at +25 °C) (Table 1).

Table 1

The quantity of aerobic bacteria (cfu/g of soil) cultivated from G10 (Kielce) and G12 (Rudki) sample, on different microbiological media

Soil sample	Temperature of culture	Microbiological medium					
		TSA	LB	M9	MacConkey	King B	SEA
G10	25 °C	$2 \cdot 10^8$	$2.7 \cdot 10^8$	$1 \cdot 10^7$	$2.2 \cdot 10^6$	$1.2 \cdot 10^8$	$6 \cdot 10^8$
	4 °C	$1 \cdot 10^5$	$2.5 \cdot 10^5$	$7 \cdot 10^5$	$2.2 \cdot 10^6$	$1 \cdot 10^7$	$1 \cdot 10^9$
G12	25 °C	ng	ng	ng	ng	$5 \cdot 10^6$	N
	4 °C	ng	ng	ng	ng	ng	$2.2 \cdot 10^6$

N – unable to count number of microorganisms, ng – no growth.

Investigated soil samples were chemically analysed. In the G12 soil sample the presence of various metals was identified. There were also heavy metals (nickel, copper, zinc, cobalt and others) among them. Attention is paid on high content of iron and manganese ions (Fig. 2).

Presence of the increased concetration of heavy metals in soil from Rudki (G12 sample) probable affects the amount and structure of bacterial microflora occuring in this environment. It is known, that such pollution can reduce intensity of the majority of biochemical reactions in soil [11, 12]. Heavy metals decrease activity of enzymes produced by soil bacteria like: urease, acid and alkaline phosphatase, amidase and nitrate reductase [13].

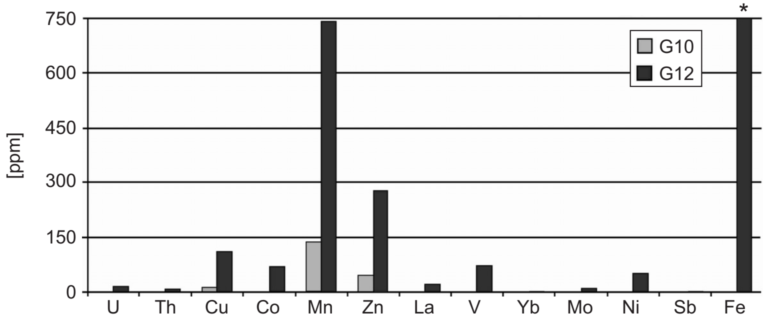

Fig. 2. Chemical analysis of soil samples; * – 156274 ppm.

For the analyzed soil samples the total ureolytic, proteolytic and lipolytic activities were determineted (Fig. 3).

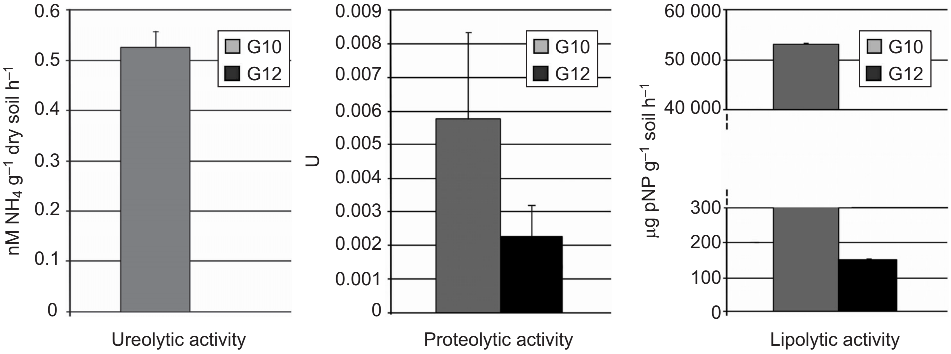

Fig. 3. The total ureolytic, proteolytic and lipolytic activities of G10 and G12 soil samples

Ureolytic activity was totally inhibited in soil highly contaminated by heavy metals (G12 sample). This observation is consistent with previous data [13]. Also Nawaguo *et al* observed, that bacterial urease is especially sensitive to heavy metals presence [14].

In both soils very weak (in G12 at the detection limit) proteolytic activity was noted. Blaszak and Nowak [15] observed the opposite phenomenon. In their studies after soil contamination, only proportions of proteolytic bacteria, which maintained its activity, was varied. However, in this case, in the laboratory conditions only copper ions added to soil samples had toxic activity [15]. In presented studies soil was contaminated by different metals in varying degrees already at the time of samples collection. Therefore, is impose here conclusion, that the presence of various toxic agents is significant. This is confirmed with studies Lopez *et al*, where the inhibitory effect of heavy metals on bacterial proteolytic enzymes activity was also observed [16].

In G10 and G12 samples lipolytic activity was observed, however in G12 sample this activity was significantly lower. In G12 sample, collected from pyrite mine area in Rudki, the presence of cobalt, nickel and zinc was detected. It is known, that presence of heavy metals inhibits the activity of this enzyme, and cobalt and nickel have a very strong inhibitory effect [17].

There are data, where negative effects of heavy metals on biochemical activity as well as the number and growth of soil bacteria was observed. However, the presence of a relatively rich bacterial microflora (on soil extract agar) allow to hope for the possible bioremediation of these soils.

Conclusions

1. Soil bacteria present in environment highly contaminated by heavy metals have specific nutritional requirements, what causes that they can not be effectively cultured on standard microbiological media. For efficient cultivation of these microorganisms is necessary to supplement the media with compounds found in their natural habitat.
2. The presence of heavy metals, including uranium, have an inhibitory effect on the general soil biochemical activity.
3. Heavy metals presence abolish urease activity in soil.

Acknowledgements

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ANALIZA ILOŚCIOWA TLENOWYCH BAKTERII HODOWALNYCH ORAZ CAŁKOWITEJ AKTYWNOŚCI ENZYMATYCZNEJ GLEBY URBICENOZY KIELC I RUDEK

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Abstrakt: Wykonano badania mikrobiologiczne i biochemiczne dwóch próbek gleb miejskich województwa świętokrzyskiego (Kielce, Rudki). Celem pracy była analiza ilościowa tlenowej hodowalnej mikroflory bakteryjnej oraz określenie całkowitej aktywności enzymatycznej gleby z okolic o dużym natężeniu ruchu drogowego (Kielce) i terenów byłej kopalni pirytu (Rudki), skąd wydobywano rudę uranową. Do izolacji drobnoustrojów zastosowano pożywki komercyjne (TSA, agar LB, MacConkey'a, M9 i King B) oraz podłoża z ekstraktami glebowymi. Hodowlę prowadzono w dwóch temperaturach: +25 °C i +4 °C. W przypadku gleby urbicenozy Kielc, na pożywkach komercyjnych zaobserwowano większą ilość drobnoustrojów hodowanych w temperaturze +25 °C (od 10 do 10^8 razy więcej w zależności od stosowanej pożywki), natomiast na podłożu z ekstraktem glebowym niemal 2 razy więcej bakterii rosło w temp. +4 °C. W glebie zanieczyszczonej uranem (Rudki) obfity wzrost drobnoustrojów hodowanych w obu temperaturach występował jedynie na agarze z ekstraktem glebowym. Oznaczono również całkowitą aktywność ureolityczną, proteolityczną i lipolityczną próbek glebowych. W przypadku próbek gleby z Kielc obserwowano wszystkie badane aktywności, natomiast dla gleby z Rudek tylko lipolityczną.

Słowa kluczowe: bakterie glebowe, metale ciężkie, całkowita aktywność enzymatyczna

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COMPARISON OF THE ANTIOXIDANT PROPERTIES OF SELECTED EDIBLE SPROUTS FROM THE CRUCIFERAE FAMILY

PORÓWNANIE WŁAŚCIWOŚCI ANTYOKSYDACYJNYCH WYBRANYCH JADALNYCH KIEŁKÓW Z RODZINY KRZYŻOWYCH

Abstract: Germinating seeds of the Cruciferae family are a natural source of valuable nutrients. The aim of this study was to compare the antioxidant properties of selected edible sprouts of the Cruciferae family using different methods. We tested seeds of broccoli, white mustard, red cabbage and cardamine purchased from PNOS Ozarow Mazowiecki S.A. The seeds germinated on Petri dishes lined with filter paper in natural light conditions at 22 °C, with no added nutrients. Aqueous extracts from the seedlings were prepared according to the method described by Zielinski and Kozlowska. Three methods were used to measure the total antioxidant capacity of the extracts: one using ABTS, one by Brand-Williams et al based on the properties of DPPH, and one using DMPD. Antioxidant content was expressed in μM of Trolox per 1g fresh weight of seedlings. Substantial differences were found in the antioxidant properties of the extracts tested. The highest values were obtained using the DMPD and ABTS methods. The richest sources of antioxidants were the extracts from red cabbage and white mustard sprouts in the first day of growth. The extract from the cardamine sprouts had the lowest antioxidant properties. The antioxidant content in the seedlings decreased with growth time. The results presented indicate which sprouts have the highest antioxidant properties as well as the optimal time for consuming them.

Keywords: Cruciferae family, total antioxidant capacity, ABTS, DPPH, DMPD

Introduction

Sprouts are a natural source of nutrients, dietary fiber, vitamins and microelements. The low cost of growing them, the availability and variety of seeds, and their beneficial effects on human health are all arguments in favour of including them in our daily diet. Nevertheless, they are still undervalued as a dietary constituent which could replace

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synthetic supplements. They are popular among people practising a vegetarian lifestyle. The sprouts consumers most prefer include those of mung beans, broccoli, cardamine, lentils, radishes, grains, alfalfa, pumpkin, sunflower, soy and maize. Due to the variety of seeds and of the sprouts obtained from them, they are a source of diverse taste sensations and, most importantly, of compounds with health-promoting effects. Sprouts contain significantly more concentrated nutrients than seeds or adult plants. The high-molecular-weight reserve substances (proteins, carbohydrates and fats) accumulated in seeds are broken down during the germination process into simple compounds that are easily assimilated by the human body. In addition, enzymes taking part in the breakdown of these substances facilitate digestion of food eaten together with sprouts. Most sprouts contain more vitamin C, polyphenols and B vitamins than mature vegetables, and exhibit higher antioxidant activity as well [1].

Regular consumption of sprouts provides protection against many serious illnesses, activates the immune system, corrects vitamin and mineral deficiencies, and most importantly, has anticarcinogenic effects. It has been estimated that an appropriate diet and lifestyle can prevent 30–40 percent of tumours [2]. Epidemiological studies show that a diet deficient in compounds with anticarcinogenic properties (e.g. tocopherols, ascorbic acid, selenium, polyphenols and isothiocyanates) may contribute to the occurrence of tumours more than the presence of carcinogenic compounds in the diet (e.g. heterocyclic amines and aflatoxins). Plants of the Cruciferae family are particularly recommended as a source of natural antioxidant compounds. Cruciferous plants contain substantial quantities of vitamins, minerals and dietary fibre [3]. They are rich in essential minerals such as Ca, Cu**,** Zn, P, Mg, Na, K, Fe and others [4, 5]. There is significantly more Ca, Mg, Cu and Zn in edible sprouts than in seeds. Ready-to-eat sprouts contain on average 12 % more Ca, 14 % more Mg, 25 % more Cu and 45 % more Zn than seeds [3].

Sprouts are also contain considerable amounts of dietary fibre, which are beneficial mainly to the peristalsis of the digestive tract. The total content of dietary fibre in ready-to-eat seedlings is significantly higher than in seeds [3].

The aim of the study was to compare the antioxidant activity of selected edible seedlings of plants of the Cruciferae family: broccoli, white mustard, red cabbage and cardamine. In recent years numerous methods have appeared in the literature for determining the presence or concentration of antioxidant compounds. Among the most frequently used are spectrophotometric techniques, which assess the total antioxidant potential of the substances tested. In the present study, three different spectrophotometric methods were used to measure the antioxidant activity of seedling extracts. In each of these methods a coloured indicator substance reacts with the antioxidants contained in the sample, and the decrease in absorbance is proportional to the content of compounds with antioxidant properties.

Total antioxidant capacity in the seedling extracts was determined using ABTS cation radical [6, 7] and antioxidant activity was assessed using the method of Brand-Williams et al [8], based on properties of DPPH. Also used to determine antioxidant activity was the DMPD method described by Fogliano et al [9].

Materials and methods

Materials

Chemicals

2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), *1,1-diphenyl-2-picrylhydrazyl* (DPPH), and *N,N-Dimethyl-p-phenylenediamine* (DMPD) were purchased from Sigma; Trolox from Aldrich, potassium persulfate ($K_2S_2O_8$) from Sigma-Aldrich and ethanol and iron(III) chloride from POCH. All chemicals and reagents were analytical grade or purest quality.

Plant material

For the study we used seeds of broccoli, white mustard, red cabbage and cardamine purchased – from PNOS Ozarow Mazowiecki S.A.

The seeds germinated in Petri dishes lined with filter paper, in natural light conditions, at 22 ^{o}C, with no added nutrients [10]. The seeds were watered daily. Material for testing was collected on days 1 to 6. Aqueous extracts from the seedlings were prepared according to the method described by Zielinski and Kozlowska [11]. For each aqueous extract 10 grams of seedlings and 100 cm^3 of water were used. The seedlings were homogenized with water and the homogenate was centrifuged. The extracts were diluted 5-fold. All extracts were prepared in three replications.

Methods

Determination of ABTS radical scavenging activity

The ABTS method for assessing antioxidant activity is based on determination of the reduction of ABTS$^{\bullet+}$ produced beforehand in a reaction of ABTS with potassium persulfate. To prepare the ABTS$^{\bullet+}$ stock solution, 7 cm^3 of phosphate buffer (0.1 M, pH = 7.4), 19.5 mg ABTS and 3.3 mg of potassium persulfate were used. The solution was left in the dark at room temperature for 12–16 hours. The ABTS$^{\bullet+}$ solution obtained was diluted so that the absorbance at λ = 414 nm was 1.0 [7].

50 mm^3 of the seedling extracts were added to 1500 mm^3 an ABTS$^{\bullet+}$ cation radical solution. When the antioxidants contained in the extract reduce the ABTS$^{\bullet+}$ cation radical to colourless ABTS, they cause the solution to lose its blue-green colour, with the decrease in the intensity of the colour dependent on the antioxidant content in the sample. Absorbance of the solution was measured 30 minutes after the reaction was initiated, at a wavelength of 414 nm [7]. Antioxidant activity was calculated as a percentage of ABTS$^{\bullet+}$ cation radical inhibition. The results were expressed as μM of Trolox per 1 g fresh weight. All determinations were made in at least three independent replications.

Determination of DPPH radical scavenging activity

The DPPH assay was done according to the method of Brand-Williams et al [8] with some modifications. A 0.05 mM DPPH solution was prepared by dissolving 19.71 mg of DPPH in 100 cm^3 of ethanol. The solution obtained was diluted so that its absorbance at $\lambda = 517$ nm was 1.0. The solution was stored in the dark.

50 mm^3 of the seedling extracts were added to 1500 mm^3 of an ethanol solution of DPPH. The mixture obtained was left in the dark at room temperature for 30 minutes. When DPPH reacts with an antioxidant, the stable DPPH radical takes on electrons from the antioxidant and loses its intense violet colour. The decrease in absorbance was measured in relation to the control sample (DPPH solution + ethanol) 30 minutes after the reaction was initiated, at a wavelength of $\lambda = 517$ nm. Antioxidant content was expressed as μM of Trolox per 1g fresh weight. All determinations were made in at least three independent replications.

Determination of DMPD radical scavenging activity

The method using the reagent DMPD is based on generation of a coloured DMPD cation radical in an oxidant solution (Fe^{3+}). The cation radical loses its colour as a result of the transfer of a hydrogen atom from the antioxidant. A DMPD solution (100 mM) was prepared by dissolving 209 mg of DMPD in 10 cm^3 of deionized water, and then 1 cm^3 of this solution was added to 100 cm^3 of 0.1 M acetate buffer (pH 5.25). DMPD cation radical was obtained by adding 0.2 cm^3 of 0.05 M iron(III) chloride solution.

50 mm^3 of the seedling extracts were added to 1500 mm^3 an $DMPD^{\bullet+}$ cation radical solution. The decrease in absorbance was measured in relation to the control sample 30 minutes after the reaction was initiated, at a wavelength of $\lambda = 505$ nm [12]. Antioxidant content was expressed as μM of Trolox per 1 g fresh weight. All determinations were made in at least three independent replications.

Results and discussion

Observation of the germination process showed that the seeds differed in terms of the time, energy and rate of germination, as well as the sensory values of the sprouts. Testing of antioxidant content was begun after one day of growth; at this time the seeds were swollen and some of the seed coats had split. On the first day of growth most of the seeds had already produced a radicl. According to our observations, sprouts on days 4 and 5 of growth were best for consumption. Other authors have also emphasized that sprouts have the best sensory characteristics after 4 days of growth in the dark, when they contain bioactive compounds such as L-ascorbic acid, reduced glutathione, inositol phosphates, phenolic compounds and tocopherols [13]. Moreover, in a study by Zielinski et al, in the seeds of all species investigated the greatest accumulation of tocopherols was found to occur after the 4th and 5th days of germination in light. Tocopherol content on subsequent days (up to day 7) remained constant [14].

The antioxidant activity of the aqueous extracts of the sprouts was measured by different methods. Due to differences in the reactions taking place in each method, the measurements had different results, even though the content was expressed as Trolox equivalent.

Substantial differences were found in the antioxidant properties of the extracts tested (Fig. 1–3). One-day-old seedlings have the highest antioxidant content, but would be difficult to eat due to their small size. In the ABTS method, the highest antioxidant content was noted in one-day-old seedlings of white mustard (34.89 ± 0.88 μM trolox · g^{-1}) and red cabbage (34.42 ± 1.28 μM trolox · g^{-1}); antioxidant content was lower in the broccoli seedlings (30.99 ± 0.92 μM trolox · g^{-1}), and the lowest in the cardamine (16.29 ± 0.82 μM trolox · g^{-1}).

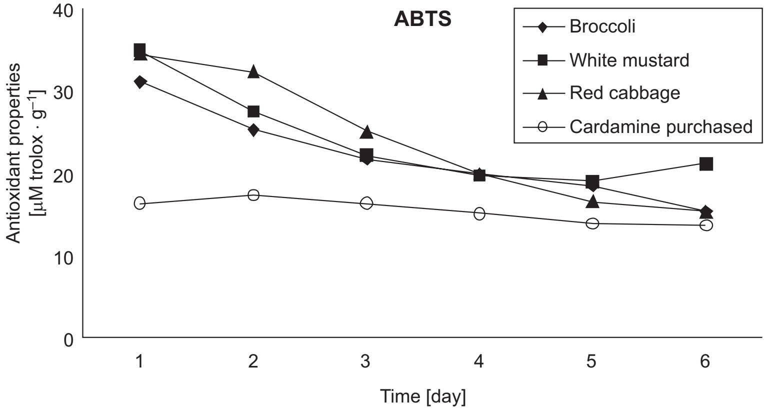

Fig. 1. Change in antioxidant content in seedlings of plants of the Cruciferae family determined by the ABTS method

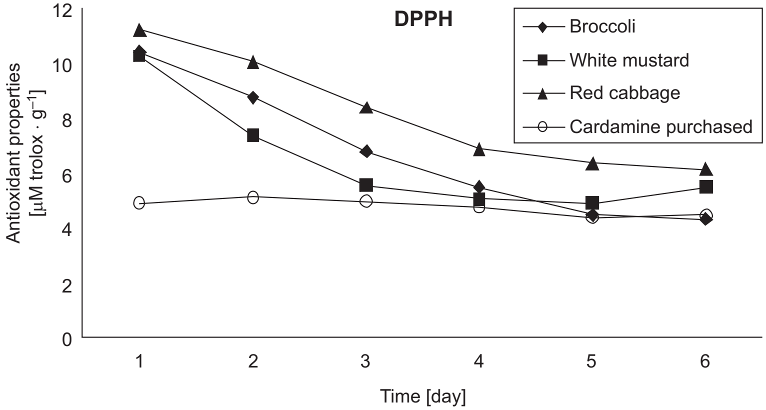

Fig. 2. Change in antioxidant content in seedlings of plants of the Cruciferae family determined by the DPPH method

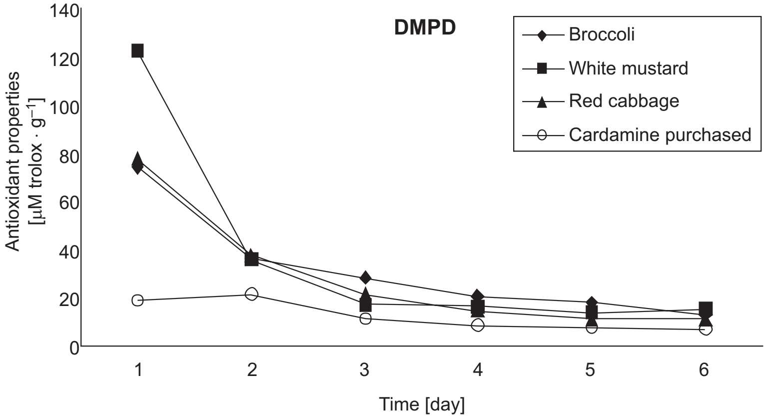

Fig. 3. Change in antioxidant content in seedlings of plants of the Cruciferae family determined by the DMPD method

The highest values were obtained using the DMPD and ABTS methods. The richest sources of antioxidants were the extract from white mustard (122.52 ± 8.66 μM trolox · g^{-1}), red cabbage (77.54 ± 3.15 μM trolox · g^{-1}) and broccoli (74.02 ± 5.85 μM trolox · g^{-1}) prepared on day 1 of growth. The extract from the cardamine sprouts (18.47 ± 0.13 μM trolox · g^{-1}) had the lowest antioxidant properties. The numerical values obtained using the various assays differ due to the specificity of the reactions of the indicator substances with the antioxidants. Similar results were obtained using the ABTS and DMPD methods: the same seedlings had the highest or the lowest antioxidant content. A different ranking of antioxidant content was obtained using the DPPH method: the highest was noted in red cabbage (11.18 ± 0.73 μM trolox · g^{-1}) and the least in cardamine (4.89 ± 0.21 μM trolox · g^{-1}), while the level of antioxidants found in white mustard seedlings (10.22 ± 0.46 μM trolox · g^{-1}) was similar to that in broccoli (10.37 ± 0.44 μM trolox · g^{-1}).

The antioxidant content of the seedlings decreased with the time of growth (Fig. 1–3). However, between days 3 and 5 of growth sprouts attain the appropriate size and are recommended for consumption. Other authors have also confirmed that the best sprouts to eat are obtained on the third, fourth or fifth day, *ie* when they attain optimum properties for consumption [15].

Antioxidant content measured using the ABTS method in the sample taken between days 1 and 6 of growth decreased by about 55 % in the case of red cabbage, 40 % for white mustard, 17 % for cardamine and 51 % for broccoli. Similar results were obtained with the DPPH method. The DMPD method was considerably more sensitive; the initial antioxidant content was found to decrease by about 86 % in the red cabbage extract, 87 % in the white mustard, 65 % for the cardamine and 82 % for the broccoli.

The methods used in this study to determine antioxidant activity are relatively simple and fast. They are often used in determining the total antioxidant capacity of extracts from plants and other biological material [16]. The results of measurements of antioxidant capacity depend on the type of method used, but for the same method they are highly repeatable. Barton et al draw attention to the speed with which the antioxidants react with the indicator substance. The results obtained by different methods for testing total antioxidant capacity do not reflect the content of all reactive antioxidant components present in the sample. The greater the speed of the reaction, the higher the results obtained by the method. According to these authors, the FRAP method includes the most components, while the DPPH method only some of the most reactive ones, and the ABTS method yields intermediate values. For this reason the lowest numerical values are obtained in the DPPH method [17]. Comparison of the data obtained in the present study confirms these observations: DPPH yielded the lowest numerical values and ABTS intermediate values.

Schlesier et al point out that while it is difficult to compare results obtained using different methods of measuring antioxidant capacity, results obtained using one test in strictly defined conditions are repeatable and comparable. It is strongly recommended to use at least two methods due to the differences between the test systems [18, 19]. Acetone-water, ethanol-water, methanol-water, or water solutions are most often used for extraction [20]. The method of preparing the extract also affects the final result of the assay, so this should always be taken into account in comparing data. One of the criteria that should be applied is the bioaccessibility of the extract [21]. In the present study, aqueous extracts were used because they are inexpensive to prepare and can be used directly for consumption or further production processes without the need to remove methanol or acetone from them.

Sprouts are becoming an important element of the human diet, which is reflected in numerous scientific publications, including those concerning TEAC measurements. However, it is difficult to compare data obtained by different laboratories due to the lack of standardization of methods for measuring TEAC. The DPPH method has been used to compare the antioxidant activity of ethanol extracts from the sprouts of wheat, lentils, sunflower, radishes, and mung beans. The richest source of antioxidants was the sunflower sprout extract, while a lower level of antioxidants was found in the radish sprout extract. The remaining extracts had similar, low TEAC [15].

It is worth noting that while total antioxidant content decreases, the concentration of particular antioxidant compounds can increase. This was confirmed by Zielinski et al, who found that vitamin B_1 (thiamine) content in white mustard seeds is higher than in 4-day ready-to-eat sprouts, while vitamin B_2 (riboflavin) content increases with growth [3]. The authors showed that vitamin B_1 content in the seeds of selected cruciferous plants – small radish, radish, rapeseed and white mustard – ranged from 0.41 to 0.70 mg/100 g d.m, while the amount of this vitamin in the sprouts was 46, 39, 42 and 47 % lower, respectively. Vitamin B_2 content in the sprouts is approximately three times higher than in the seeds. Vitamin B_2 content in the seeds ranges from 0.096 mg/100 g^{-1} d.m to 0.138 mg/100 g^{-1} d.m. [3]. The authors confirm that germinating seeds of cruciferous plants are also an excellent source of microelements and fibre. Moreover, cruciferous plants are a good source of vitamins C, E and K [22]. γ-Tocopherol was found to be the main contributor of vitamin E content in cruciferous sprouts [14]. Zielinski and Kozlowska demonstrated that a 100-gram portion of 4-or-5-day-old sprouts produced from the seeds of the cruciferous plants they tested, or a mixture of them, can provide 15.3–21.6 % of the daily requirement of vitamin E for men and 19.1–29.5 % for women [14].

Plants of the Cruciferae family are rich in glucosinolates – secondary metabolites with anticarcinogenic activity [23]. Other anticarcinogenic compounds occurring in Cruciferae include quercetin [24], isothiocyanates [25] and selenium [26], as well as Se-methylselenocysteine and 1,2-dithiole-3-thione [27].

Plants from the cruciferae family are particularly recommended as sources of natural antioxidant compounds providing protection against lifestyle diseases. Consumption of plants from the Cruciferae family reduces the risk of various types of cancer, including tumours of the lungs [28], colon [29], prostate [30] and many others. Consumption of cruciferous plants has been shown to better protect against cancer than other fruits and vegetables [31].

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PORÓWNANIE WŁAŚCIWOŚCI ANTYOKSYDACYJNYCH WYBRANYCH JADALNYCH KIEŁKÓW Z RODZINY KRZYŻOWYCH

Wydział Nauk Rolniczych w Zamościu
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Kiełkujące nasiona roślin Krzyżowych są naturalnym źródłem cennych składników odżywczych. Celem pracy było porównanie różnymi metodami właściwości antyoksydacyjnych wybranych jadalnych kiełków z rodziny kapustowatych. W badaniach zastosowano nasiona brokuła, gorczycy białej, kapusty czerwonej i rzeżuchy zakupione w firmie PNOS w Ożarowie Mazowieckim S.A. Nasiona kiełkowały na szalkach Petriego wyłożonych bibułą filtracyjną, w naturalnych warunkach oświetlenia, w temperaturze 22 ^{o}C, bez dodatku składników odżywczych. Wodne ekstrakty z siewek przygotowano wg metody opisanej w pracy Zieliński i Kozłowska. Do pomiaru całkowitej zdolności antyoksydacyjnej ekstraktów z siewek zastosowano trzy metody: metodę ABTS, metodę Brand-Wiliams i współpr. opartą o właściwości DPPH oraz metodę z DMPD. Zawartość antyoksydantów wyrażano w mmolach troloxu na 1 g świeżej masy siewek. Badane ekstrakty znacznie różniły się właściwościami przeciwutleniającymi. Najwyższe wartości pomiarów uzyskano w metodzie DMPD i ABTS. Najbogatsze źródło przeciwutleniaczy stanowił ekstrakt z kiełków kapusty czerwonej i gorczycy białej sporządzony w pierwszym dniu hodowli. Ekstrakt z kiełków rzeżuchy charakteryzował się najniższymi właściwościami przeciwutleniającymi. Zawartość antyoksydantów w siewkach spadała w miarę czasu trwania hodowli. Prezentowane wyniki badań umożliwiają wskazanie kiełków o najwyższych właściwościach antyoksydacyjnych, a także pozwolą wybrać optymalny czas ich spożycia.

Słowa kluczowe: rodzina Krzyżowych, całkowita zdolność antyoksydacyjna, ABTS, DPPH, DMPD

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EFFECT OF INDUSTRIAL WASTE DUMPS ON THE QUALITY OF RIVER WATER

WPŁYW SKŁADOWISK ODPADÓW PRZEMYSŁOWYCH NA JAKOŚĆ WÓD RZECZNYCH

Abstract: Landfills are an important source of industrial pollution of surface and groundwater area in the vicinity of waste heaps. Hydrosphere pollution is mainly a consequence of the formation of leachate with high concentrations of toxic substances. In addition to substances considered as a typical toxic materials such as cadmium and lead, leaching water may contain high concentrations of other ions. These include the sulfates, chlorides and sodium. The paper presents the results of landfill leachate of colliery waste tip "Panewniki" located in the catchment of river Jamna (Mikolow). Post coal mine waters are characterized by very high electrical conductivity, which ranges from 7.5 to 8.3 mS · cm^{-1} in the case of the first effluent and from 7.9 to 10.6 mS · cm^{-1} in the case of the second effluent, respectively. Such high values of conductivity are caused by leaching of waste deposited in a heap. As a result of leaching process the increase of the concentration of individual ions also occurs. These can include sodium and chloride. The maximum sodium concentration may exceed the 2500 mg · dm^{-3} and 560 mg · dm^{-3} chlorides.

Inflow of effluents into the river Jamna affects significant changes in water quality. The statistically significant differences in the concentrations of sodium and chloride in the waters above and below Jamny flow of leachate were demonstrated.

Keywords: leachate, landfill, water pollution, river, water quality

The chemical composition of river waters is dependent on many factors. Amongst most important ones are: type of bedrock and climate [1]. It can undergo spatiotemporal changes. The concentration of ions has an impact on discharge [2].

In last decades inflow of pollution both from point, linear and surface sources increased considerably [3, 4]. Especially landfills as industrial waste tips in some areas are important sources of water pollution.

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Hydrosphere pollution in these type of sites is mainly a result of creation of leachate with high concentration of toxic substances as lead cadmium. There are high contents of other ions as sulphures, chlorides and sodium. This study focus on the influence of leachate of colliery waste tip "Panewniki" on quality of water Jamna in Mikolow near Katowice (Silesian Upland) (Fig. 1).

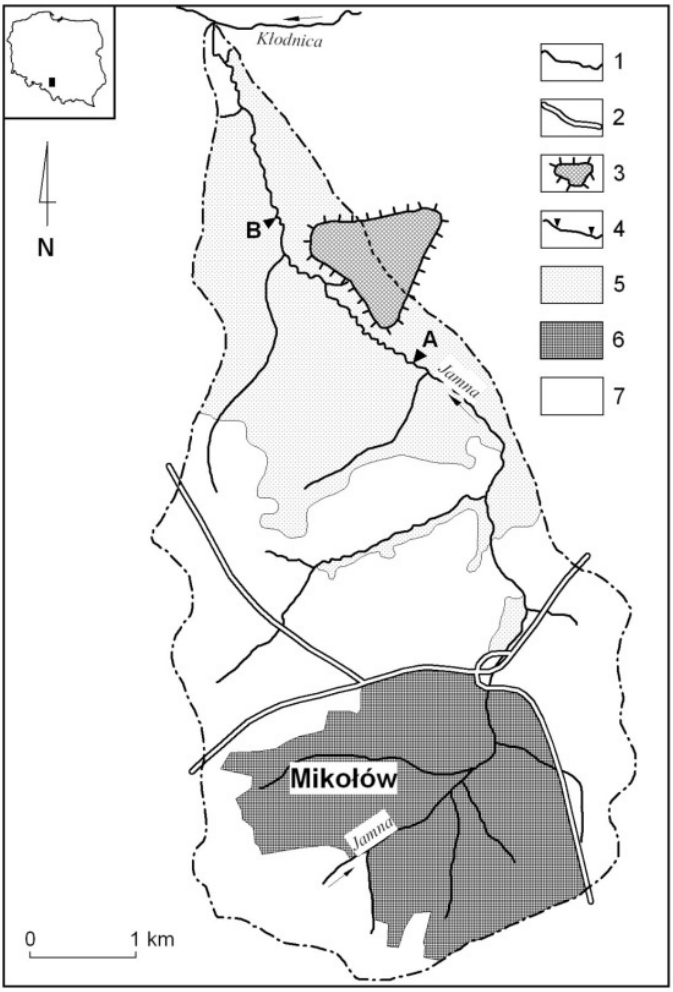

Fig. 1. Localization of dumping "Panewniki" [9]: 1 – Water courses, 2 – Roads, 3 – Dumping, 4 – Points of water sampling, 5 – Forest, 6 – Build- up area, 7 – Fields

Material and methods

The hydrogeographical mapping aiming at estimation of water relations of waste tip was carried out according to methodological assumptions by [5]. The measurement of pH, temperature, conductivity as well were performed in the field by the device Multi – Line P – 4. The determination of selected ions was done according to methods of hydrochemical studies [6, 7].

The measurements of flow intensity were performed by RBC flume for water discharge measurement by Eijkelkamp company. To determine how leachate waters affect the quality of Jamna river waters two study plots were located in river. The study site "3" was placed above outflow and study site "4" below inflow of leachate waters. Also in sites of leachate outflows two study sites "1" and "2" were established (Fig. 2).

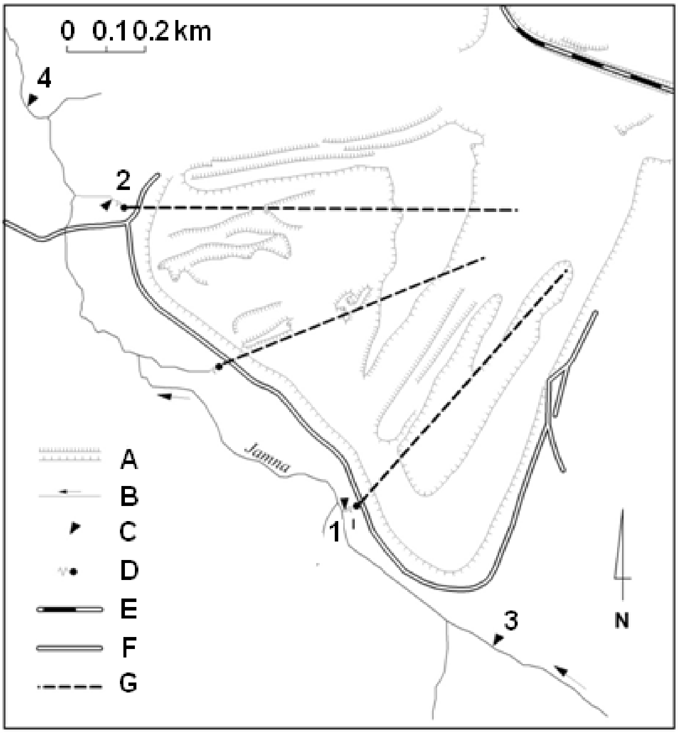

Fig. 2. Localization of inflow of leachate waters of the landfill "Panewniki": A – margins of the waste heap, B – water courses, C – points of water sampling: 1–4, D – outflows of leachate waters, E – railways, F – roads, G – buried old drainage system of canals

For the purpose of statistical analyses data gathered in the years 2002–2008 (minimal number of observations n = 12) were employed. Statistical analyses of obtained data was carried out using free statistical software R (R development Core Team 2011). In graphs, the following description of study sites was used: 1, 2 – leachates of Panewniki landfill and 3, 4 – study sites located in Jamna river.

For the purpose of the study Jamna river which is situated in Katowice Uplandwas was chosen. Jamna is a left tributary of Klodnica river and its length is estimated to be about 12 km. In the lower part of catchment, the coal mine "Panewniki" landfill of wastes is located (Fig. 1). It is an aboveground waste heap. The object is characterized by concentrated outflows of leachate waters. These kind of outflows are formed most frequently where deposition of wastes leads to fulfilling of river valleys [8].

In this case there is a different situation. The studied waste heap was created in the site of former sandpit, which after cessation of exploitation was filled by mine wastes (Fig. 3). The deposition of wastes did not finish when landfill was leveled. The wastes were deposited further and leveled-aboveground landfill was formed 13 m high. The

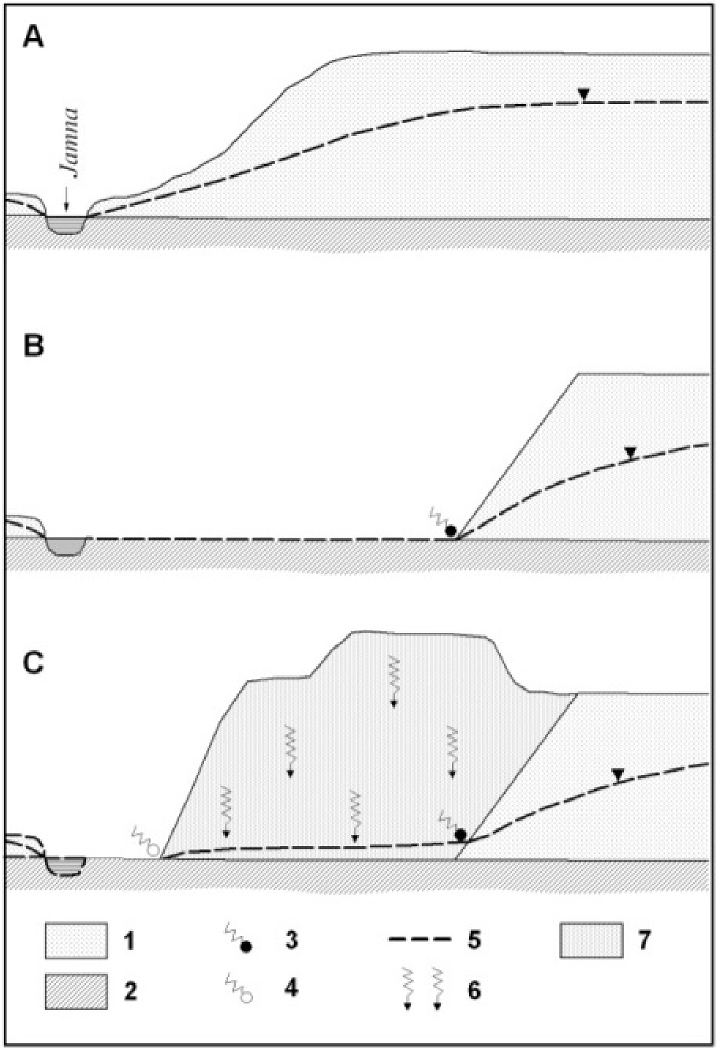

Fig. 3. Changes in relief and water relations within waste tip “Panewniki” [9]: A – State in 1950 before sand exploitation, B – state in 1970 during sand exploitation, C – present state in 2010; 1 – sands with gravel, 2 – boulder clay, 3 – outflows of underground waters, 4 – leachate, 5 – water level of underground waters, 7 – barren rocks

surface of the waste tip amounted to ca 118 ha. The introduction of effluents is at site of intersection between the block and topographic surface of the bottom of former drainage canals in sandpits (Fig. 3). In the landfill there are two permanent leachate outflows. In this waste tip apart from infiltration waters the resource of leachate are underground waters flowing from the margin of depression funnel. Perhaps underground waters are bigger part in the balance of leachate waters than infiltration waters.

Results and discussion

The leachate waters of the studied landfill are characterized by very high electric conductivity which varies from 7.2 to 8.3 mS · cm^{-1} in the case of "1" and 7.9 to 10.6 mS · cm^{-1} respectively in study site "2" (Fig. 4). So high values of conductivity are caused by leaching of deposited wastes on the landfill. There are statistically differences in conductivity of leachate waters both in terms of space and time.

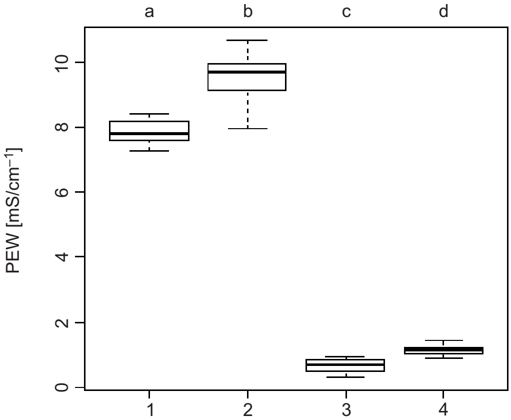

Fig. 4. Comparison of PEW between particular leachate waters of the landfill "Panewniki". The small different letters above mean that mean values differ significantly at $p < 0.05$

Coefficient of variation (Cv) for site "1" amounts to 26 % and for "2" – 32 %. For a comparison in natural springs value of this coefficient does not extend a few percent [9]. Also in waters of Jamna river above the landfill value of this coefficient was low and amounted to 6 %. Inflow of leachate waters to river Jamna influence their conductivity.

Conductivity increased significantly in waters of Jamna below inflow of leachate (Fig. 4). The value of coefficient of variation increased to 17 %.

As a result of leaching, the concentration of particular ions increased as well. These are sulphates, chlorides and sodium. Amongst wastes of coal mine industry are sulphates [8, 10, 11]. Their source are pirytes FeS_2, because anion S^{2-} in moist environment in anaerobic conditions is being oxidized to SO_4^{2-} [12].

The concentration of this ion in leachates varied between 4160 to 5730 mg · dm^{-3} (Fig. 5). In case of sulphates there were no significant differences in particular leachates. Such differences were observed in river Jamna (Fig. 5). Inflow of leachate caused the increase of contents of sulphates in waters of Jamna from 5 % in study site "3" to 15 % in "4".

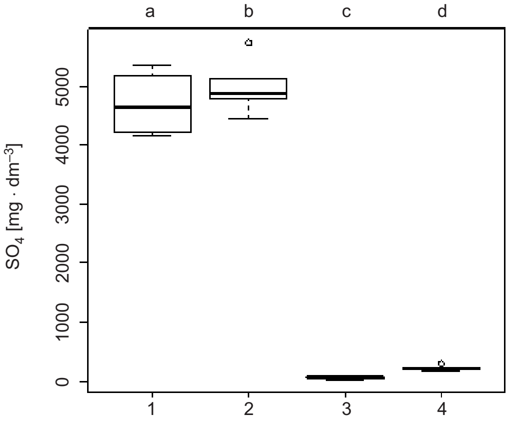

Fig. 5. Comparison of sulphates between particular leachate waters of the landfill "Panewniki". The small different letters above mean that mean values differ significantly at $p < 0.05$

In the case of chlorides and sodium the similar influence on quality of waters in Jamna was observed. Below inflow of leachate there was statistically higher concentration of studied ions (Fig. 6, 7). In case of sodium the value of variation coefficient increased from 3 % in study site 3 to 11.4 % in study site 4. There were no statistically significant differences in potassium concentration above and below leachate waters inflow (Fig. 8). It may be explained by relatively low concentration of potassium in leachate waters which is 85 mg/dm^{-3} on average. However, below the inflow greater variation of potassium concentrations (Cv = 9.4 %) than above the inflow (Cv = 7.5) can be noticed.

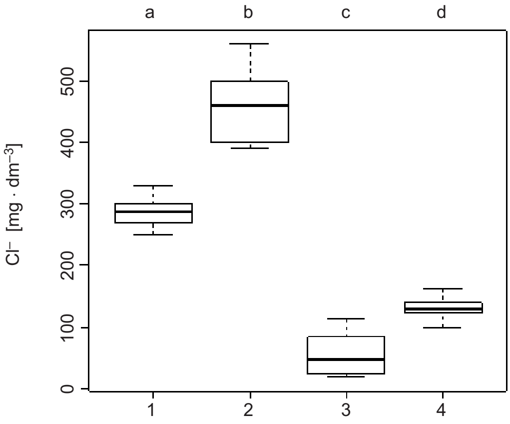

Fig. 6. Comparison of chlorides between particular leachate waters of the landfill "Panewniki". The small different letters above mean that mean values differ significantly at $p < 0.05$

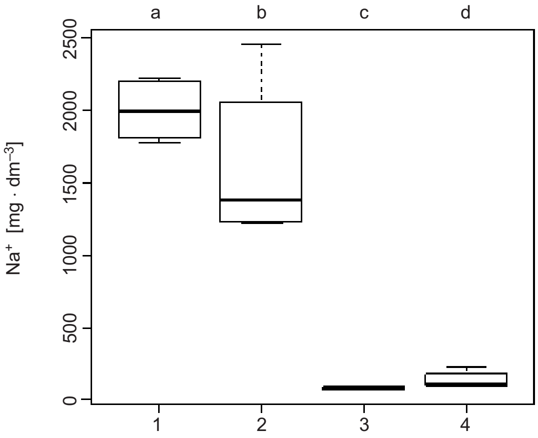

Fig. 7. Comparison of sodium between particular leachate waters of the landfill “Panewniki”. The small different letters above mean that mean values differ significantly at $p < 0.05$

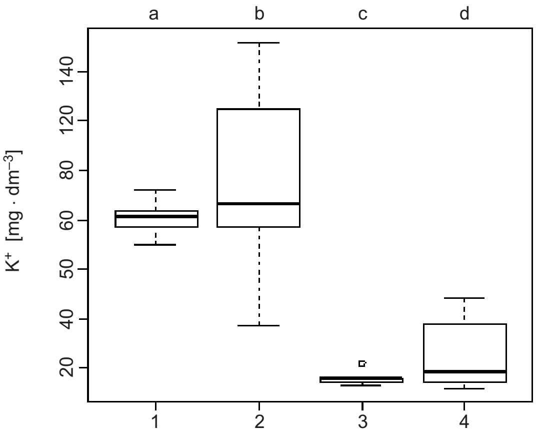

Fig. 8. Comparison of potassium between particular leachate waters of the landfill “Panewniki”. The small different letters above mean that mean values differ significantly at $p < 0.05$

Conclusions

The obtained results let to draw the following conclusions:

– leachate waters of colliery waste tips are characterized by high conductivity and high contents of SO_4^{2-}, Cl^-, Na^+ and K^+;

– inflow of leachate to Jamna river does not lead to the increase of K^+ concentration in its waters;

– inflow of leachate to river Jamna lead to increase of conductivity and high contents of SO_4^{2-}, Cl^- and Na^+ in its waters;

– inflow of leachate lead to higher variation of high concentrations of SO_4^{2-}, Na^+ and K^+ in waters of river Jamna;

– the landfills of coal mine wastes can be considered as surface and permanent sources of pollution of surface waters.

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WPŁYW SKŁADOWISK ODPADÓW PRZEMYSŁOWYCH NA JAKOŚĆ WÓD RZECZNYCH

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Abstrakt: W artykule przedstawiono wpływ składowiska odpadów przemysłowych na jakość wód rzeki Jamny. Wykazano, że wody odciekowe charakteryzuje bardzo dużą konduktywnością elektryczną oraz wysokim stężeniem jonów SO_4^{2-}, Cl^-, Na^+ oraz K^+. Jest to następstwo ługowania zdeponowanych na składowisku odpadów. Dopływ odcieków do rzeki Jamny powoduje wzrost konduktywności elektrycznej jej wód oraz stężenia jonów SO_4^{2-}, Cl^- oraz Na^+. Tym samym składowiska odpadów przemysłowych stanowią trwałe ognisko zanieczyszczenia wód powierzchniowych.

Słowa kluczowe: zanieczyszczenie wód, wody odciekowe, składowiska odpadów, jakość wód rzecznych

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TRACE ELEMENTS IN THE BOTTOM SEDIMENTS OF THE IRKUTSK RESERVOIR

PIERWIASTKI ŚLADOWE W OSADACH DENNYCH ZBIORNIKA IRKUCKIEGO

Abstract: The chemical composition of bottom sediments of the Irkutsk Reservoir was examined. Ten sediment samples collected at different depths in four sectors of the Reservoir were analysed in a laboratory. Concentrations of 30 trace elements were determined. The purpose of the study was to assess the anthropogenic impact on the Reservoir geosystem. Barium and zirconium had the highest concentration in the sediments. Concentrations of certain elements varied spatially, while those of others were similar in all the sectors sampled. The highest element concentrations were usually found in sector 3 (in the vicinity of Novogrudinina). Maximum concentrations for around a dozen elements exceeded the geochemical background level for sedimentary rocks and the soil environment. Irkutsk Reservoir sediments exhibited a high concentration of chromium when compared with sediments from various other reservoirs impounded by dams. The study has shown that the environment of the Irkutsk Reservoir is subject to local and regional anthropogenic impact.

Keywords: Irkutsk Reservoir, Lake Baikal, bottom sediments, trace elements, heavy metals

The functioning of water bodies involves the development of morphogenetic processes leading to their terrestrialisation [1–3]. In areas where water bodies are fed by rivers, deltas form [4–6], and in the littoral zone, the material produced by the erosion of shores accumulates [7–9]. At the same time, a layer of sediments forms on the entire bottom of the water body [10–12]. This is a result of sedimentation and sedentation

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processes [13, 14]. Sedimentation is the process whereby material settles out of the water under the influence of gravity. On the other hand, sedentation is the accumulation of organic matter as a result of growth in vegetation within the water body. In reservoirs impounded by dams, bottom sediments mostly form as a result of sedimentation; the waters of the rivers that feed the reservoirs form the primary source of the material accumulated [15–17]. This is confirmed by methods for determining the extent of silting in reservoirs impounded by dams that are based on river flow characteristics [3, 18]. The age of bottom sediments in reservoirs impounded by dams usually does not exceed several decades, so these sediments are not an interesting subject for palaeogeographic studies unlike sediments in natural lakes.

Numerous substances accumulate in bottom sediments. It is often emphasised that these sediments are significant from the point of view of determining the phosphorus cycle; these form the primary environment among the components of the limnic geosystem where this element accumulates [19]. Numerous micropollutants also accumulate in sediments: trace elements (including heavy metals), polycyclic aromatic hydrocarbons, polychlorinated biphenyls, surfactants, radionuclides and others. This is related to the sorption of these pollutants by suspensions within the body of water and their deposition in the sediment material [20]. The presence of micropollutants in bottom sediments is a common subject of study both for natural lakes [21, 22] and anthropogenic water bodies, including particularly those impounded by dams [23, 24]. These studies underline the intensity and nature of anthropogenic impact on the limnic geosystem, since it is mainly human activity that determines the patterns of micropollutant migration and accumulation in the environment [25–28]. In this article, a study is described which examines the presence of trace elements in the bottom sediments of the Irkutsk Reservoir, which is impounded by a dam and fed by the waters of Lake Baikal. The purpose of the study was to determine sediment pollution and to assess the anthropogenic impact on the Irkutsk Reservoir geosystem. The study was also designed to verify the common view that the natural environment in the vicinity of Lake Baikal in the Russian Siberia exhibits low pollution levels. The bottom sediment layer of the Irkutsk Reservoir has already been the subject of studies described in the literature, *eg* with respect to modelling the transport of pollutants [29] or sedimentological zones [30, 31].

The Irkutsk Reservoir, which has operated since 1962, is the highest and at the same time the smallest reservoir of the Angara River cascade [9, 32, 33]. The Reservoir is situated on the upper reach of the Angara River, which flows from Lake Baikal (Fig. 1). It lies within a relatively straight stretch of the valley 55 km in length; its average width is 2 km. The average inflow from Lake Baikal to the Reservoir is 1,850 m^3/s, while the outflow across the dam cross-section is 1,863 m^3/s on average. The reservoir holds around 2.1 km^3 of water. Its average depth is 3.9 m in the upper section, 10.2 m in the middle section and 17.5 m in the section adjacent to the dam. Small towns and villages are situated along Reservoir shores. The city of Irkutsk from which the Reservoir takes its name is located almost entirely below the dam (Fig. 1).

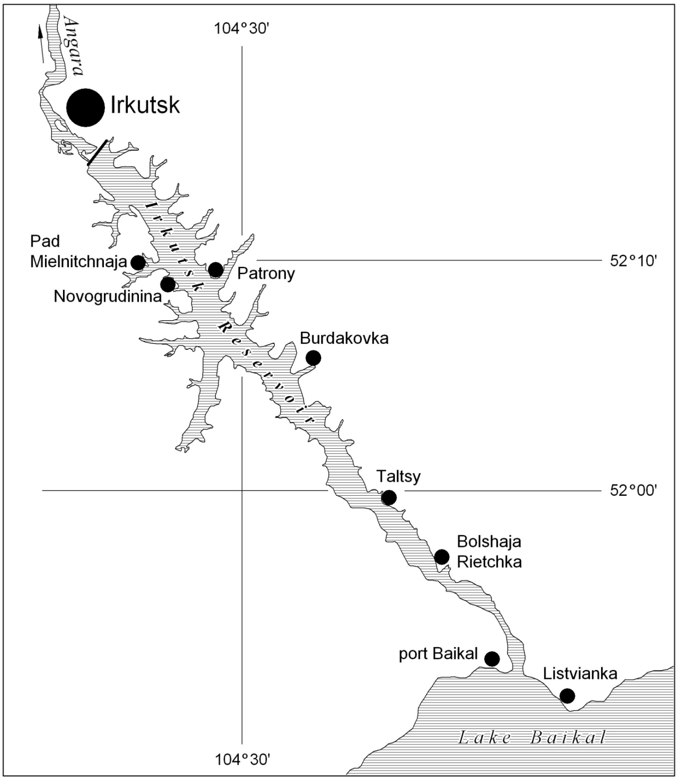

Fig. 1. The location of the Irkutsk Reservoir

Methods

Bottom sediment samples were collected from the Irkutsk Reservoir in July 2010. Samples were collected from a boat, using a sediment core sampler. Ten samples were collected in four Reservoir zones (Table 1):

– zone 1 – in the vicinity of Taltsy;
– zone 2 – in the vicinity of Patrony;
– zone 3 – in the vicinity of Novogrudinina;
– zone 4 – in the vicinity of Pad Mielnitchnaja.

Zone 1 is situated in the upper (southern) part of the Reservoir, while the other zones are in its lower (northern) part.

The sediments collected were placed in sterile plastic containers that were tightly sealed before being delivered to the laboratory. The chemical composition of sediments was analysed at ACTLABS (*Activation Laboratories* Ltd.) in Canada. Analyses were conducted to establish the concentrations of the following trace elements in the samples:

Table 1

Bottom sediment sample collection locations in the Irkutsk Reservoir

Zone	Number of sample	Coordinates		Depth [m]
		latitude	longitude	
1	1	52° 00′ 00.3″ N	104° 39′ 49.7″ E	1.5
	2	51° 59′ 51.9″ N	104° 39′ 44.4″ E	3.0
2	3	52° 09′ 46.4″ N	104° 27′ 22.5″ E	2.0
	4	52° 09′ 38.1″ N	104° 27′ 15.6″ E	1.0
	5	52° 09′ 35.0″ N	104° 27′ 12.4″ E	7.0
3	6	52° 09′ 23.6″ N	104° 25′ 08.7″ E	15.0
	7	52° 08′ 43.7″ N	104° 25′ 18.3″ E	3.5
	8	52° 09′ 12.5″ N	104° 25′ 12.0″ E	0.7
	9	52° 08′ 45.6″ N	104° 25′ 26.3″ E	12.0
4	10	52° 09′ 57.6″ N	104° 22′ 47.6″ E	1.0

Ba, Be, Sr, V, Y, Zr – the FUS-ICP (*fusion-inductively coupled plasma*) method; Cd, Cu, Mo, Ni, Pb, Zn – the TD-ICP (total digestion-inductively coupled plasma) method; Ag, As, Co, Cr, Cs, Hf, Hg, Rb, Sc, Th, U, La, Ce, Lu, Nd, Sm, Eu, Yb – the INAA (*instrumental neutron activation analysis*) method. Element concentrations are given in ppm.

Results and discussion

The sediments examined began to form at the very beginning of the Reservoir's existence. They are a polygenetic material that was supplied by the waters of the main tributary (the Angara), by tributaries within the direct catchment area, from the littoral zone, from the atmosphere (atmospheric deposition) and from the body of water itself (the sedimentation of autochthonous plankton). In the case of the Irkutsk Reservoir, whose catchment exhibits a dispersed human activity pattern, all the sources listed above should be considered responsible for the supply of trace elements. The impact of individual pollution sources on the environment is considered where a certain type of anthropogenic pressure is concentrated and intensive [34–37].

Laboratory analyses determined the presence of numerous trace elements in the bottom sediments examined. Among the 30 elements covered by the study, only silver, cadmium, mercury and molybdenum were not detected (Table 2). The possible concentrations of these elements did not exceed the detection threshold of the method used. The presence of individual elements in the sediment material varied widely. Highest concentrations were recorded for barium (607.3 ppm, *ie* 0.06 % on average) and zirconium (355 ppm, *ie* 0.03–0.04 %). There were also significant amounts of strontium – 233.6 ppm on average (*ca* 0.02 %), chromium – 160 ppm on average (slightly below 0.02 %), vanadium – 123 ppm on average (slightly above 0.01 %), cerium – 103 ppm on average (ca. 0.01 %) and zinc – 84.9 ppm on average (slightly below 0.01 %). Some elements were present in concentrations of at most several parts per million. These were arsenic, beryllium, caesium, europium, samarium, uranium and ytterbium. Lutetium content did not exceed 1 ppm.

Table 2

Presence of trace elements in Irkutsk Reservoir bottom sediments

Element	Zone 1 (samples 1–2)	Zone 2 (samples 3–5)	Zone 3 (samples 6–9)	Zone 4 (sample 10)
	[ppm]			
Ag	< 0.5	< 0.5	< 0.5	< 0.5
As	6–7	7–10	8–9	5
Ba	623–633	595–606	582–615	613
Be	2	2	2	2
Cd	< 0.5	< 0.5	< 0.5	< 0.5
Ce	93–106	85–108	96–151	97
Co	16–17	19–23	18–20	18
Cr	104–123	147–194	148–243	146
Cs	5.7–6.8	3.7–5.3	2.7–5.1	2.8
Cu	21–22	21–34	23–31	22
Eu	1.9–2.3	1.8–2.3	1.7–3.0	1.8
Hf	6.7–7.0	6.3–15.8	7.1–22.9	9.7
Hg	< 1	< 1	< 1	< 1
La	42.7–44.4	47.9–60.0	48.7–75.9	44.6
Lu	0.51–0.58	0.56–0.76	0.53–0.92	0.64
Mo	< 2	< 2	< 2	< 2
Nd	33–45	29–46	35–58	26
Ni	44–48	63–80	60–74	53
Pb	15–16	13–17	15–16	16
Rb	50–90	60–70	40–80	50
Sc	16.0–17.2	17.2–18.9	17.7–18.5	15.5
Sm	5.9–6.4	5.8–7.3	5.8–9.6	5.8
Sr	200–210	186–264	208–274	268
Th	6.7–7.1	7.8–9.9	8.1–12.9	7.1
U	3.4–4.8	2.5–3.3	2.1–4.3	3.4
V	107–108	123–140	124–137	101
Y	27–29	30–38	30–48	34
Yb	3.7–3.8	4.2–5.5	3.9–7.0	4.6
Zn	93–98	73–94	73–93	92
Zr	200–204	200–601	231–863	330

The concentrations of certain elements in the bottom sediments were highly variable depending on where the sample in question was collected. For example, zirconium concentrations ranged from 200 ppm to 863 ppm, while those of hafnium (6.3; 22.9) ppm. On the other hand, certain elements (*eg* cobalt, lead, scandium) were present in similar concentrations in all samples, *ie* their concentrations did not vary spatially (Table 2). This points to the presence of local, anthropogenic sources of selective pollution. For example, study zones Nos. 2 (in the vicinity of Patrony) and 3 (in the vicinity of Novogrudinina) exhibited higher chromium, nickel, vanadium and zirconium concentrations. In general, the highest levels of trace element pollution were found in zone 3, where the maximum concentration for almost half of the elements covered by the study was recorded. Element concentrations in the bottom sediments of zone 4 (the vicinity of Pad Mielnitchnaja) were close to the average for all samples or lower.

The concentrations of the trace elements analysed in the bottom sediments of the Irkutsk Reservoir often exceeded their natural levels in sedimentary rocks or soil (Table 3) [38]. Average concentrations of elements in sediments were higher than the geochemical sedimentary rock background for cerium, chromium, europium, hafnium, scandium and zirconium, while maximum concentrations exceeded the geochemical background for cobalt, neodymium, thorium, uranium, vanadium and ytterbium as well. Natural levels were also exceeded with respect to soil concentrations of the trace elements under consideration. The bottom sediments sampled contained higher levels of around a dozen elements analysed (Ce, Co, Cr, Eu, La, Lu, Nd, Ni, Sc, Sm, Y, Yb) than the natural soil environment. The element concentrations measured in bottom sediments were additionally compared with the legally admissible limits for the surface layer of arable soil in Poland (Table 3) [39]. Those limits were exceeded for barium and chromium while cobalt concentrations oscillated around the admissible value. Thus the bottom sediments analysed could not be used as arable soil in Poland.

The presence of certain trace elements in the bottom sediments of the Irkutsk Reservoir in concentrations higher than those characteristic for the lithosphere and pedosphere points to the presence of anthropogenic impact on the environment of the Reservoir and its catchment. As Karnaukhova [40] states, the waters of Lake Baikal are the main source of trace elements that find their way into the Irkutsk Reservoir. These elements are most probably introduced into water together with the pollutants dumped from the industrial and urban centres located on the southern shores of Lake Baikal as well as with atmospheric deposition. Atmospheric deposition should be considered a major source of trace elements not only in industrial and urban areas but also in the peripheries of urban and industrial centres [41] and even in areas that are situated at a significant distance from pollution sources [42]. The area of southern Lake Baikal and the Irkutsk Reservoir is certainly affected by the influx of pollutants emitted in the nearby Irkutsk–Cheremkhovo Industrial Region and in other industrial centres in the southern part of Eastern Siberia. The supply of trace elements to the Irkutsk Reservoir also occurs within its direct catchment. This is evidenced by the increase in the concentrations of certain elements in the waters of the Angara River during its flow through the Reservoir [40]. It is suspected that the supply of elements is the result not only of the dumping of pollutants from human settlements but also of the chemical denudation of the soil and rock environment.

Table 3

Concentrations of trace elements [ppm] in Irkutsk Reservoir bottom sediments compared with their concentrations in the lithosphere and pedosphere

Element	Irkutsk Reservoir bottom sediments		Sedimentary rocks [38]	Soils [38]	Arable soil [39]
	average value	maximal value	most frequent value	average value	permissible value in Poland
Ag	< 0.5	< 0.5	0.05–0.25	0.03–0.10	—
As	7.7	10	1–13	0.2–16.0	20
Ba	607.3	633	50–800	20–1000	200
Be	2	2	0.2–6.0	0.4–4.3	—
Cd	< 0.5	< 0.5	0.035–0.300	0.20–1.05	4
Ce	103	151	7–90	48.7	—
Co	19	23	0.1–20.0	8	20
Cr	160	243	5–120	7–150	150
Cs	4.5	6.8	0.5–10.0	0.1–26.0	—
Cu	26.4	34	2–60	1–140	150
Eu	2.1	3	0.2–2.0	1.23	—
Hf	10	22.9	0.3–6.0	21[1]	—
Hg	< 1	< 1	0.04–0.40	0.05–0.30	2
La	52	75.9	4–90	26.1	—
Lu	0.6	0.92	0.2–1.2	0.34	—
Mo	< 2	< 2	0.14–2.60	0.7–4.0	10
Nd	39	58	4.7–41.0	19.5	—
Ni	62.3	80	5–90	6[2]	100
Pb	15.3	17	3–40	25–40	100
Rb	65	90	5–200	lack of data	—
Sc	18	18.9	0.5–15.0	2–12	—
Sm	6.5	9.6	1.3–10.0	4.8	—
Sr	233.6	274	20–600	5–1000	—
Th	8.6	12.9	1.7–12.0	6–13	—
U	3.4	4.8	0.45–4.10	1–11	—
V	123	140	10–130	11–220	—
Y	33	48	4–50	5–25	—
Yb	4.6	7	0.3–4.4	2.06	—
Zn	84.9	98	10–120	30–125	300
Zr	355	863	20–220	470[1]	—

[1] in loess soil in Russia; [2] in agricultural soil in Poland.

While analysing the presence of trace elements in the bottom sediments of the Irkutsk Reservoir, special attention should be paid to heavy metal concentrations. The presence of heavy metals best reflects the extent of anthropogenic impact, since they are introduced into the aquatic environment chiefly as a result of human activity owing to their widespread use in industry [20, 43, 44]. In Table 4, concentrations of cadmium, lead, copper, zinc, chromium and nickel in the bottom sediments of the Irkutsk Reservoir and of other reservoirs impounded by dams in other part of the world are listed [45–59].

Table 4

Heavy metal concentrations in bottom sediments of selected reservoirs impounded by dams worldwide

Reservoir	Cd	Pb	Cu	Zn	Cr	Ni
	[ppm]					
Atatürk Dam Lake (Turkey) [45]	—	—	15–23	59–61	—	44–140
Barra Bonita (Brazil) [46]	5.0–6.9	43–71	166–255	224–230	75–168	98–107
Billings Reservoir (Brazil) [47]	59 ± 8	438 ± 33	562 ± 35	1640 ± 114	802 ± 66	432 ± 41
Dillon Reservoir (USA) [48]	5–13	64–299	31–195	912–3217	—	7–51
Irkutsk Reservoir (Russia)	**< 0.5**	**13–17**	**21–34**	**73–98**	**104–243**	**44–80**
Ivankovo Reservoir (Russia) [49]	—	9–28	11–111	55–540	48–165	15–43
J.A. Alzate Reservoir (Mexico) [50]	2.0–2.8	12–76	15–61	92–233	< 50–145	15–43
Keban Dam Lake (Turkey) [51]	—	—	912–5398	1226–6592	1364–31264	833–7902
Kuibyshev Reservoir (Russia) [52]	—	26–40	42–59	100–220	—	67–180
Nasser Lake (Sudan/Egypt) [53]	3–11	12–29	9–69	30–97	5–50	92–145
Rybnik Reservoir (Poland) [54]	2–85	11–315	16–1117	51–2441	14–739	3–184
Temple (France) [55]	0.6–180	31.3–593	16.7–78	82–7230	—	—
Texoma Lake (USA) [56]	1–3	5–15	9–136	33–242	12–51	6–31
Tresna (Poland) [57]	0.0–1.7	25–62	16–36	83–177	12–56	31–66
Tuttle Creek Lake (USA) [58]	0.3–0.6	16–160	20–44	65–150	48–120	19–77
Wadi Al-Arab Dam (Jordan) [59]	6–13	—	20–190	170–960	—	—

These data show that compared with other reservoirs, small amounts of cadmium, lead, copper and zinc are present in the sediments of the Irkutsk Reservoir. Nickel concentrations in the sediments of the Irkutsk Reservoir are comparable with the levels recorded for many other reservoirs; it is only chromium concentrations in the sediments that are high in the Irkutsk Reservoir compared with other such reservoirs. Sources of chromium in the aquatic environment include effluent from many sectors of industry, domestic sewage and burning coal. Therefore, the environment of the Irkutsk Reservoir is subject to anthropogenic impact that is reflected, *inter alia,* by high chromium concentrations. The only positive aspect of this pollution pattern is the fact that chromium exhibits the lowest toxicity among the heavy metals listed and does not accumulate in aquatic organisms [44].

Conclusions

1. The operation of the Irkutsk Reservoir for almost half a century has resulted in the formation of the bottom sediment layer.
2. The sediments contained numerous trace elements, chief among which were barium and zirconium. The concentrations of certain elements (*eg* zirconium, hafnium) were similar for different Reservoir zones, while the presence of others (*eg* cobalt, lead) varied spatially to a significant extent.
3. Around a dozen elements were present in the bottom sediments examined in quantities that exceeded their natural concentrations in sedimentary rocks and in the soil environment.
4. Compared with sediments in other reservoirs impounded by dams, sediments of the Irkutsk Reservoir exhibited both high chromium concentrations and at the same time low cadmium, lead, copper and zinc concentrations.
5. The presence of trace elements in the sediments of the Irkutsk Reservoir points to the existence of local and regional anthropogenic impact on the environment of the Baikal area.

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PIERWIASTKI ŚLADOWE W OSADACH DENNYCH ZBIORNIKA IRKUCKIEGO

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Abstrakt: Badano skład chemiczny osadów dennych Zbiornika Irkuckiego. W laboratorium przeanalizowano 10 próbek osadów, pobranych w czterech sektorach zbiornika z różnych głębokości. Określono zawartość 30 pierwiastków śladowych. Celem badań była ocena wpływów antropogennych na geosystem zbiornika. W składzie osadów dominowały bar i cyrkon. Koncentracja niektórych pierwiastków była zróżnicowana przestrzennie, a innych zbliżona we wszystkich sektorach badawczych. Największe zawartości pierwiastków występowały najczęściej w sektorze 3 (w rejonie miejscowości Nowogrudinina). Maksymalne zawartości kilkunastu pierwiastków przekraczały poziom tła geochemicznego dla skał osadowych i środowiska glebowego. Na tle osadów różnych zbiorników zaporowych osady Zbiornika Irkuckiego wyróżniała duża zawartość chromu. Badania wykazały, że środowisko Zbiornika Irkuckiego podlega lokalnym oraz regionalnym wpływom antropogennym.

Słowa kluczowe: Zbiornik Irkucki, jezioro Bajkał, osady denne, pierwiastki śladowe, metale ciężkie

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INFLUENCE OF WASTE INCINERATION RESIDUE ON SLAG VITRIFICATION DURING MEDICAL WASTE UTILIZATION

WPŁYW POZOSTAŁOŚCI PO PROCESACH SPALANIA NA WITRYFIKACJĘ ŻUŻLI WYTWORZONYCH PODCZAS UNIESZKODLIWIANIA ODPADÓW MEDYCZNYCH

Abstract: Vitrification is one of many methods of ashes treatment enabling receiving products with properties like glass. The slag received after medical wastes utilization (according to Purotherme Pyrolise) is difficult material for vitrification. Obtaing the product with glass-like properties requite applying of oxygen to the zone of reaction or applying materials supporting vitrification process. In the carried out test of slag and ash after combustion process were used as additives supporting vitrification process. In effect of treatment substrat with additives vitrificators were obtained. The best quality vitrificators in result of treatment of mixture of slag from medical wastes pyrolisys process and slag from municipal wastes combustion process (30 + 70 %) and mixture of slag from medical wastes pyrolisys process and ash from municipal wastes combustion process consisting 50 % of each component were obtained. The vitrificators are characterized by amorphous structure, hardness (glass-like) 6–6.5 of scale Mohsa. Their density was above 2.6 g/cm^3. The highest density (2.924 g/cm^3) in the vitrificator obtained from mixture of slag from medical wastes pyrolisys and ash from municipal wastes combustion process was marked.

Keywords: medical wastes, pyrolisys, ash, slag, municipal wastes, combustion process, vitrification

At present the application of thermal processes for the utilization of waste becomes more and more favorable option for waste management. Thermal utilization of waste is associated with the formation of solid post processing residue, *ie* slag and ash. They can contain high concentrations of toxic substances from the input waste or formed during the process of utilization. If the amount of waste subjected to thermal utilization increases the amount of slag and ash requiring further processing will also increase. One of the methods applied for processing of waste incineration residue is vitrification [1–8]. This method allows to transform waste incineration residue into products with glass-a-like properties. Depending on the initial waste properties and applied processes

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for waste utilization the residue can show different properties and be more or less suitable for vitrification.

The slag generated during utilization of medical waste by the Purotherm Pyrolise technology (Fig. 1) was used for the investigation. Due to the specificity of pyrolisis this substrate showed high total carbon content which impairs the process of vitrification without the access of oxygen [9]. High temperature processing of the substrate in the presence of oxygen in the reaction zone can result in the formation of toxic gaseous compounds (dioxins and furans) [10]. Therefore the series of investigations was undertaken to vitrify the slag without introducing oxygen into the reaction zone. In order to do that some additional materials were used to facilitate the process of vitrification.

Fig. 1. Slag generated during the utilization of medical waste by Purotherm Pyrolise technology

Materials

Slag generated during the utilization of medical waste was subjected to the phase analysis which confirmed a significantly complex structure (heterogenic) of the substrate.

The composition of the substrate was predominated by: CaO – 27.13 %; SiO_2 – 13.7 %; MgO – 5.1 %, Al_2O_3 – 4.0 %; Na_2O – 2.85 %; Fe_2O_3 – 2.09 %. Slag showed deep gray color with black spots, non uniform granulation and contained incompletely incinerated ampoules, needles, lancets, bandage residues. The moisture content was 38 %.

To facilitate the process the selected additives, *ie* slag and ash generated from the incineration of municipal waste in a furnace, were applied. These materials showed a significant concentration of SiO_2: 48.64 % (slag) and 40.89 % (ash).

Methods

Vitrification of the substrate was conducted in the following stages:
- self-transformation of the substrate,
- transformation of the mixture of substrate and slag after incineration,
- transformation of the mixture of the substrate and ash after incineration.

The mixtures of the substrate and the additives were prepared in the ratios presented in Table 1.

Table 1

The ratios of the substrate and the additives in the mixtures subjected to vitrification [%]

Substrate	Additives	
	Slag – the mixture No. I	Ash – the mixture No. II
80	20	20
50	50	50
30	70	70

The substrate and additives were weighed and transferred into a graphite crucible which was placed into the plasma reactor. Vitrification was conducted for 12 minutes by plasma forming gas using argon with the flow velocity of 14 dm^3/min. The length of the plasma arc was 0.15 m. The I-U characteristics for the plasma reactor were selected based on the preliminary studies [1, 2].

Plasma reactor

Thermal transformation of slag and ash was conducted in the plasma reactor. The reactor is hermetic and can operate at partial pressure as well as overpressure up to 0.05 MPa which allows for conducting the process in the controlled atmosphere. The installation operates on the direct current which allows to reach the maximum arc power up to 150 kW at the regulated intensity for various voltage values. The torch inside the reactor can move vertically to alter the length of the arc up to 0.35 m. Ceramic or graphite crucibles with capacity up to 10 dm^3 can be place on the arc-furnace electrode (anode). The reactor is equipped with the observation ports made of quartz glass allowing for the observation of the reaction zone. Argon was used as a plasma forming gas. Other gas (*eg* O_2) can be introduced into the reaction zone. Exhaust gases are removed through a condenser. The installation also consists of a power supply and water cooling systems.

Results

In the course of thermal transformation of the substrate a product (Fig. 2) with a dull and partly coarse surface both at the surface and in the fracture was obtained.

During the transformation of the mixtures with slag generated during pyrolisis of medical waste and slag remained after incineration of municipal waste (the mixture No. I), the input material underwent complete melting. Only in some cases insignificant amount of the material remained in the crucible which implies that it did not undergo the reaction. In most cases, the products obtained from the mixture No. 1 showed glossy surface and the fracture. However, some of them were characterized by a non uniform structure and a coarse surface. The quality of vertified products was diverse and

Fig. 2. The product obtained after the transformation of slag generated during pyrolisis of medical waste

depended on the individual components in the mixture (Fig. 3). The best results were obtained for the mixture of 30 % of slag after pyrolisis and 70 % of slag after incineration. The vertified product (referred to as Ic) obtained from this mixture is presented in Fig. 3c.

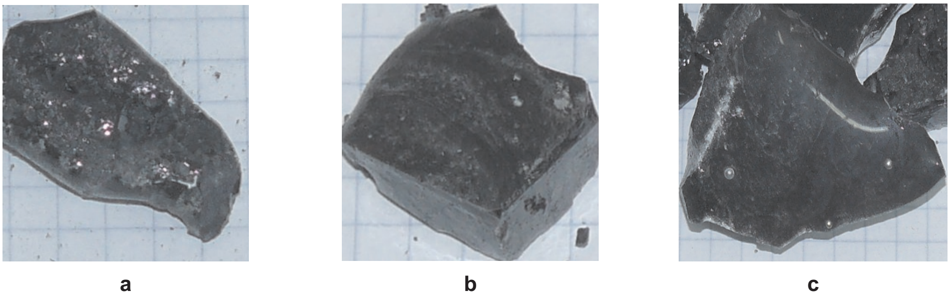

Fig. 3. The products obtained from the mixtures No. 1 (slag after pyrolisis + slag after incineration) in the following ratios: a – 80 + 20 %, b – 50 + 50 %, c – 30 + 70 %

Also, as a result of the transformation of the mixtures No. I, apart from the vertified products, a clearly separated metal fraction of the product was obtained (Fig. 4).

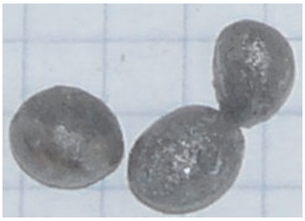

Fig. 4. Metal fraction of the product obtained during transformation of the mixture No. I

In case of the mixtures No. II (slag after pyrolisis + ash after incineration) the substrates underwent a complete reaction and were transformed into the products with the properties typical for the vertified products. They were glossy on the surface and in the fracture and had a uniform structure. The products obtained from the mixtures No. II were presented in Fig. 5. The best quality vetrified products were obtained during the transformation of the mixture containing 50 % of slag after pyrolisis and 50 % of ash after incineration. The vertified product (referred to as IIb) obtained from this mixture is presented in Fig. 5b.

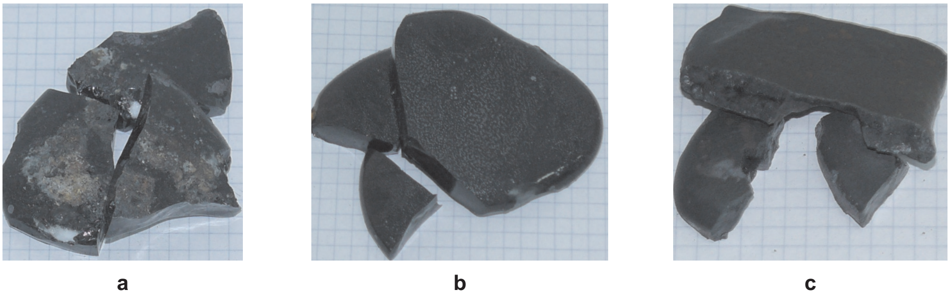

Fig. 5. The products obtained from the mixtures No. II (slag after pyrolisis + ash after incineration): a – 80 + + 20 %, b – 50 + 50 %), c – 30 + 70 %

Based on the visual analysis the best vertified products (*ie* Ic and IIb) were subjected to hardness and density tests. The results are presented in Table 2.

Table 2

Density and hardness for the selected vitrified products

Vitrified product	Density [g/cm^3]	Hardness in the Mohs scale
Ic	2.637	6.0–6.5 (decreasing to 5)
IIb	2.924	6.0–6.5

The conducted X-ray analysis of the slag after pyrolisis of medical waste (Fig. 6) and obtained vitrified products shows the transformation of the substrates into the products with amorphous structure.

Figure 7 presents the X-ray diffractogram for the vertified product Ic. The diagram shows a characteristic nub of the diffractogram for the reflection angle in the range of 20–40° which indicates the amorphous structure of the vertified product typical for glass.

Not too significant single peeks in the diagram indicate the presence of small quantities of the substances with a regular structure.

Mapping and chemical point rating analysis of the samples from the vitrified products were obtained by use of the scanning electron microscope. Figure 8 presents the EDS spectrum for the chemical composition of the glaze of the vertified products IIb and Ic. The basic compounds of the matrix glaze of these vertified products are Si, Al,O, Ca.

Figure 9 presents the morphology for the fracture of the vertified product IIb and the diversified chemical composition. The surface of the fracture is sufficiently smooth with

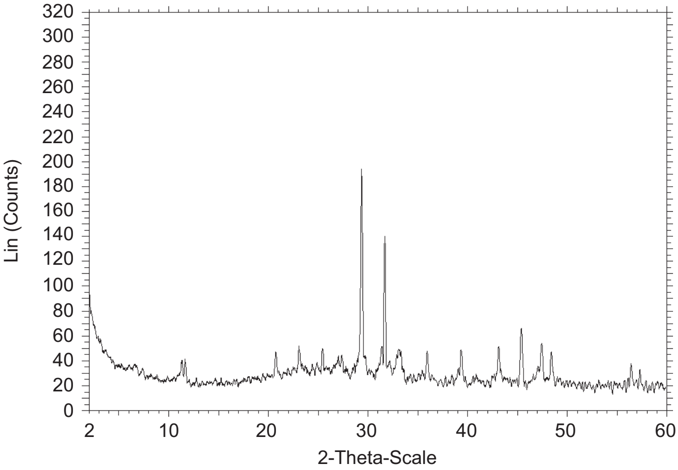

Fig. 6. The X-ray diffractogram for the slag generated during pyrolisis of medical waste

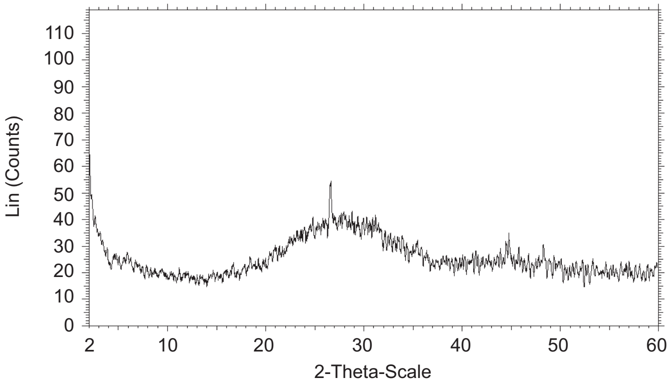

Fig. 7. The X-ray diffractogram for the vertified product Ic

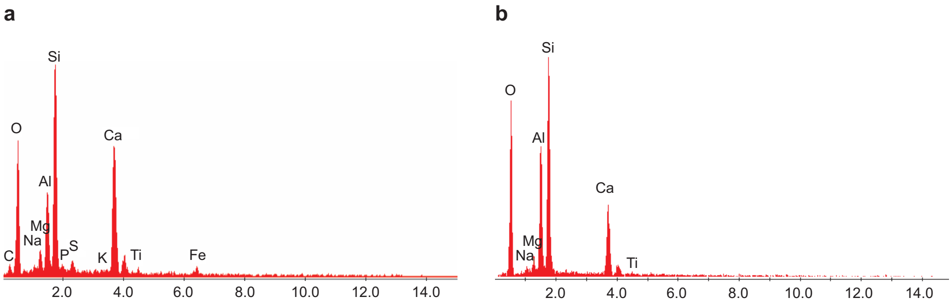

Fig. 8. The EDS spectrum of the matrix glaze of the selected vertified products: a – vertified product IIb, b – vertified product Ic

few light round segmentations. The size of these segmentations does not exceed 20 micrometers (Fig. 9 a–d).

Apart from typical glass components there are sulfur and iron in their composition (Fig. 9e). Also, apart from bright segmentations there are some spots in irregular shapes with predominant content of carbon and NaCl (Fig. 9f).

The fracture surfaces of the vetrified product Ic are more diverse. Figure 10 shows two surfaces of the fracture. One of them (Fig. 10a) is covered with numerous,

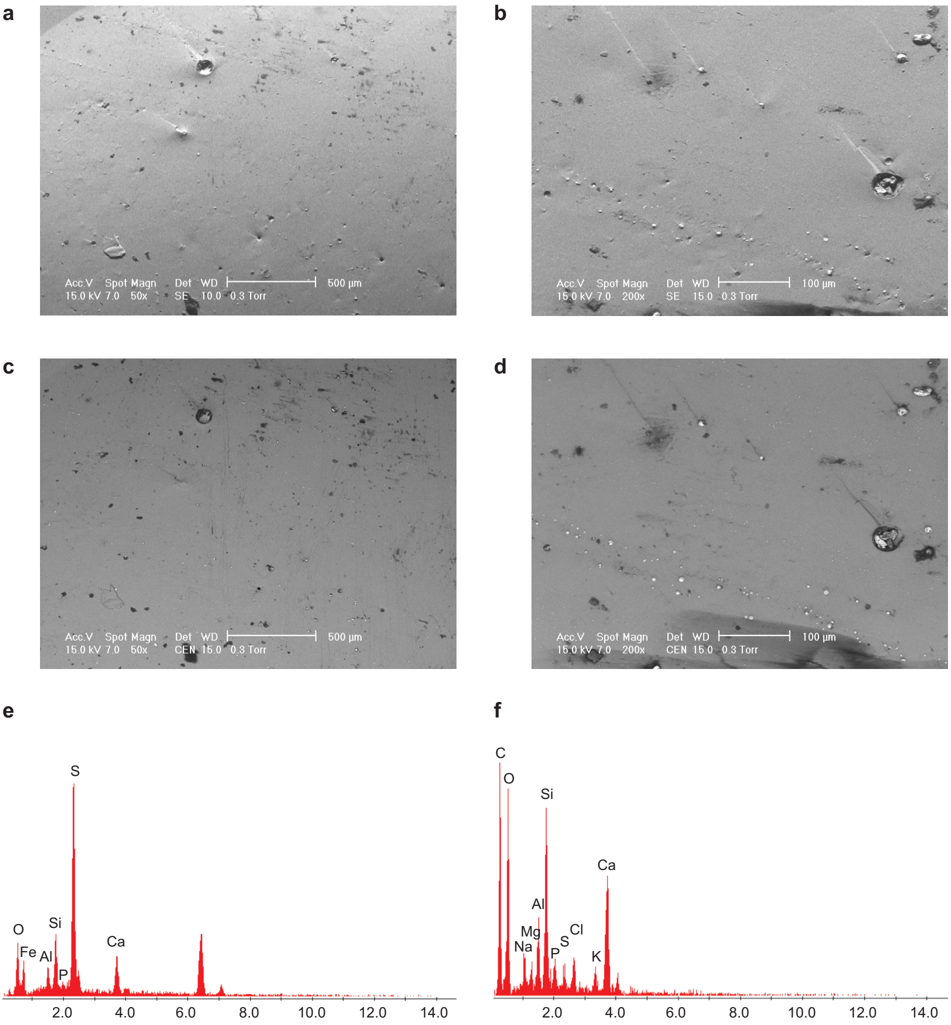

Fig. 9. The analysis of the fracture structure of the vetrified product by the scanning electron microscope: a, b – the morphology of the surface (picture taken with a secondary electron detector), c, d – the chemical composition (picture taken with a backscattered electron detector), e, f – the EDS spectrum representing the chemical composition of the segmentations (e – bright segmentations, b – dark segmentations).

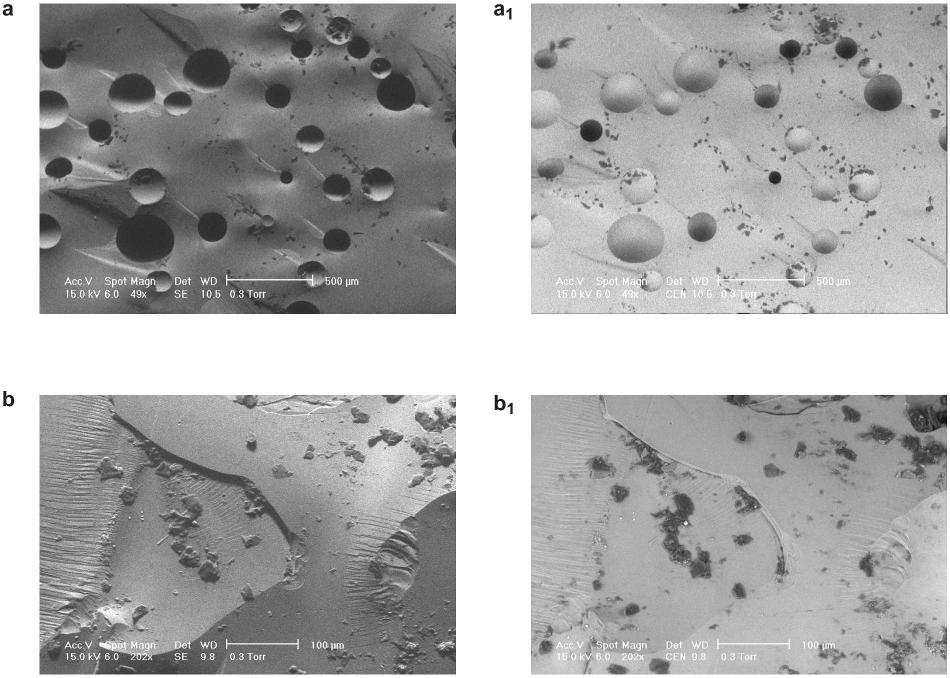

Fig. 10. The analysis of the fracture surface of the vetrified product Ic conducted with a scanning electron microscope: a, b – the morphology of the surface (the picture taken with a secondary electron detector), a_1, b_1 – the chemical composition (the picture taken with a backscattered electron detector).

half-rounded pits with a diameter from several to several hundred micrometers (about 100–300). These pits are empty and presumably are a result of the occurrence of gas bubbles. On the fracture surface (with a typical glaze composition) there are numerous dark spots and chips which are composed mainly of carbon. The morphology of the second surface is similar. Apart from the rounded pits on its surface there are some “wrinkles” (Fig. 10b), dark spots and chips composed mainly of carbon. Also, there are some small bright segmentations (up to 5 μm) which are composed mainly of potassium chloride.

Conclusions

Waste residue generated during thermal utilization of medical waste by means of the Purotherm Pyrolise technology is rather difficult to transform by vitrification. Obtaining a good quality vetrified product requires introducing oxygen into the reaction zone or the addition of selected materials which facilitate the process.

The vetrified products obtained during the transformation of the mixtures of slag and ash after incinerating municipal waste show amorphous structure typical for glass. Similarly, the hardness and density characteristics of the vetrified products are typical for glass. The main components of the glaze were: Si, Al,O, Ca. Insignificant pockets of S, Fe, C, NaCl and KCl were observed in the matrix.

The transformation of the mixtures of the substrate and slag after incineration resulted in vetrified products with different quality due to the composition of the mixture. The best quality vetrified products were obtained from the transformation of the mixture containing 30 % of slag after pyrolisis and 70 % of slag after incineration. The hardness of the vetrified products obtained from this mixture was in the range of 6–6.5 according to Mohs scale with a decreasing tendency towards 5. The density of the vetrified product Ic was 2,637 g/cm^3.

The morphology reflection of the fracture surface showed numerous empty pits (with a diameter in the range of (100; 300) μm and some small spots which had different composition than the matrix.

The transformation of the mixture of the substrate and ash after incineration resulted in the products with smooth and uniform surface. The best results were obtained for the mixture containing 50 % of slag after pyrolisis and 50 % of ash after incineration. The hardness of the vetrified products obtained from this mixture were in the range of 6–6.5 according to the Mohs scale. The density of the vetrified product IIb was 2.924 g/cm^3. The morphology reflection of the fracture surface examined with a scanning electron microscope showed smooth surface with few small segmentations.

The results of the study lead to the following conclusions:

1) good quality vetrified products from slag generated during pyrolisis of medical waste can be obtained after vetrification of the mixtures containing slag from pyrolisis and solid residue from incineration of municipal waste:

- in case of the mixtures containing slag generated after pyrolisis of medical waste and slag after incineration of municipal waste, the quality of the obtained vitrified products improves with the increase in the content of slag from incineration in the mixture whereas the best results were achieved for the mixture containing these components in the ratio of 30 % and 70 %; the pits remained after the occurrence of gas bubbles can indicate that the time of vitrification was too short,
- as for the transformation of the mixture containing slag after pyrolysis of medical waste and ash from incineration of municipal waste the best results were achieved for the mixtures with ratios of 50 % of each of the components, increasing or decreasing the content of these components deteriorates the quality of the obtained products,

2) the hardness of the vetrified products can be compared to the hardness of glass; in case of some vetrified products obtained during the transformation of the mixtures No. I, the hardness was lower (about 5 according to Mohs scale) than for the vetrified products obtained from the mixtures No. II,

3) the density of the vetrified products obtained from both types of mixtures was above 2.6 g/cm^3 reaching 2.924 g/cm^3 – which is typical for quartz glass – for the vetrified product obtained from the mixture of slag after pyrolisis and ash after incineration,

4) in case of the transformation of the mixtures containing slag after the pyrolisis of medical waste and slag from incineration of municipal waste, the recovery of metallic components is possible,

5) the addition of ash after incineration of waste allows for better results during the vitrification of slag after pyrolisis of medical waste than the addition of slag after incineration,

6) the best quality vitrified products were obtained from the transformation of the mixture containing slag after pyrolysis and ash after incineration in the ratio (by mass) of 50 % and 50 %, respectively.

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WPŁYW POZOSTAŁOŚCI PO PROCESACH SPALANIA NA WITRYFIKACJĘ ŻUŻLI WYTWORZONYCH PODCZAS UNIESZKODLIWIANIA ODPADÓW MEDYCZNYCH

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Abstrakt: Witryfikacja może być jedną z metod przekształcania stałych pozostałości po procesach termicznych, umożliwiającą uzyskanie z odpadów produktów o właściwościach szkłopodobnych. Żużel wytworzony w procesie unieszkodliwiania odpadów medycznych wg technologii Purotherm Pyrolise jest materiałem trudnym do witryfikacji. W celu ułatwienia procesu zeszkliwienia w badaniach zastosowano materiały wspomagające. Żużel po pirolizie odpadów medycznych przekształcano z pozostałościami po spalaniu odpadów komunalnych w piecu rusztowym. Najlepsze efekty osiągnięto przekształcając mieszanki zawierające 30 % żużla po pirolizie i 70 % żużla po spalaniu odpadów komunalnych oraz mieszanki zawierające 50 % żużla po pirolizie i 50 % popiołu po spalaniu odpadów komunalnych. Twardość uzyskanych witryfikatów była porównywalna do twardości szkieł i mieściła się w zakresie 6–6,5 w skali Mohsa. Gęstość witryfikatów otrzymanych z obydwu typów mieszanek wynosiła powyżej 2,6 g/cm^3, osiągając wartość 2,924 g/cm^3 w przypadku witryfikatu uzyskanego z mieszanki żużla po pirolizie i popiołu po spalaniu.

Słowa kluczowe: odpady medyczne, piroliza, popiół, żużel, odpady komunalne, spalanie, witryfikacja

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INVESTIGATION ON THE PHOSPHATE ROCK DISSOLUTION PROCESS BY PARTIAL ACIDULATION (PAPR METHOD) USING SULFURIC AND PHOSPHORIC ACID

BADANIA NAD CZĘŚCIOWYM ROZKŁADEM FOSFORYTU (METODĄ PAPR) Z ZASTOSOWANIEM KWASU SIARKOWEGO I FOSFOROWEGO

Abstract: The results of few factors on the each form of phosphates content in the PAPR-type fertilizer preparations were presented. Type of mineral acid, its concentration, amount and fineness were taken into account. Investigation was carried out with the recommendations enclosed in Regulation (EC) No 2003/2003 of the European Parliament and the Council on 13.10.2003 related to fertilizers, test methods for the phosphate content evaluation in fertilizers.

Keywords: partially acidulated phosphate rocks (PAPR), mineral acids, phosphate fertilizers, available P

One of the most popular fertilizers are phosphate fertilizers, mainly superphosphates – single and triple superphosphate which varies in the substrates used in the manufacture process. Traditional and main phosphorus source for phosphate fertilizers production process are phosphate rocks which differs in phosphorus compounds content expressed as a P_2O_5. Phosphate fertilizer manufacture process is based on treating grinded phosphate rocks (in the form of meal) with mineral acid. Main types of acids used in the manufacture process are sulfuric and phosphoric acid. As a result of phosphate raw material dissolution with phosphoric acid, triple superphosphate is being produced. When using sulfuric acid, single superphosphate is being produced. Main difference between triple and single superphosphate is phosphorus compounds content expressed as a P_2O_5. In triple superphosphate it is about three times higher than in the

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single superphosphate. Reason for this phenomenon is that phosphoric acid constitutes for additional phosphorus source in fertilizer. Depending on acid amount used in the fertilizer manufacture process, acidulation could be complete or partial. Complete acidulation takes place when the amount of acid used in the process is stoichiometric to calcium content in phosphate raw material. If the amount of acid is lower than stoichiometric to calcium content (usually 30–50 % amount of acid needed to complete dissolution) acidulation is partial [1]. Products manufactured with lower amount of acid are called PAPR fertilizer (PAPR – Partially Acidulated Phosphate Rock). Phosphate fertilizer production depends on raw material supply. One of the most important phosphate rocks suppliers, which supply main part of Polish market is Morocco and Tunisia. Rapid phosphate fertilizer market crash in 2008, caused prices increase of about 1000 % [2]. Fluctuations in the fertilizer market caused phosphate rocks output decrease and as a consequence fertilizer production decrease, which has caused fertilizer prices increase. As a result, buying possibility was limited to farmers. To avoid situation which has taken place in 2008, it is justified to search cost-effective, alternative fertilizers for conventional superphosphates, which can be used in the Polish climatic conditions. Recent trends in fertilizer market are focused on possibility of using partially acidulated phosphate rocks (PAPR – type fertilizers) as an alternative phosphorus source for crops in Poland. PAPR – type fertilizers are PAPR – partially acidulate phosphate rocks and preparations based on SSP or TSP – phosphate rocks mixtures, which differs in production process. PAPR are made by treating phosphate rock with less than the stoichiometric amount of acid needed for complete acidulation of apatite structure in the raw material [3]. Manufacture process of superphosphate – phosphate rock mixtures is based on mechanical blending of superphosphate and phosphate rock. Incomplete dissolution of apatite structure in both type of fertilizers makes them able to supply adequate dose of phosphorus in the whole plant growth cycle, because they contain both water soluble and insoluble phosphorus compounds. In the first phase of plant growth only water soluble compounds are available [4–6]. In the next phases, as a result of metabolic processes of microorganisms, water insoluble forms are becoming available for plants. There is a lack of data concerning PAPR – type fertilizers use in the modern climate of Central Europe, especially in Poland, whereas PAPR – type fertilizers are widely used in climate conditions of Australia, New Zealand where they show same agronomic effectiveness as conventional superphosphates [1, 7, 8].

Materials and methods

Research on the partial acidulation of Tunisia phosphate rock and the influence of acid type, amount and concentration, raw material fineness and also alterations in the phosphorus content in time for each product were presented. PAPR – type fertilizes were made using Atlas Syrris apparatus equipped with hotplate, teflon vessel and aluminium coating allowing to control temperature, stirring intensity and time of the process. Fertilizers were obtained using Tunisia phosphate rock, containing about 28.5 % P_2O_5. Phosphorus content in each product was being analyzed in the day of its manufacture and after 2, 4, 7, 10, 14 days. The influence of fineness on partial acidulation process was investigated by sampling two following fractions: 125–160 and 250–500 μm. Phosphoric and sulfuric acids were taken into consideration in examination of acid type influence on phosphorus compound content in products. Three values of degree of PAPR stoichiometric norm (η_{PAPR}) were taken into consideration: 0.3; 0.5; 0.7. Degree of PAPR stoichiometric norm determines amount of acid used in the process in proportion to acid required for complete acidulation of apatite structure of phosphate rock. Examination of the acid concentration influence on phosphorus compounds content was carried out using two values of concentration for each acid. For sulfuric acid it was 65 and 75 mass percent and for phosphoric acid it was 62 and 69 mass percent Manufactured PAPR type fertilizers were compared with fully acidulated reference samples (η_{PAPR} = 1). Analyzes of phosphorus content in fertilizers were carried out with the recommendations enclosed in Regulation (EC) No. 2003/2003 of the European Parliament and the Council on 13.10.2003 related to fertilizers, test methods for the phosphate content evaluation in fertilizers [9].

Results and discussion

Table 1 presents PAPR – type fertilizers manufacture process parameters in lab-scale. Results of the analysis of water soluble and available phosphorus compound in ratio to total phosphorus content of selected fertilizers were presented.

Table 1

Fertilizers manufacture process parameters

Fineness [μm]	Acid conc. [% w/w]	Acid type	Product number and η_{PAPR}
125–160	75	sulfuric	P1(η_{PAPR} = 0.7), P2(η_{PAPR} = 0.5), P3(η_{PAPR} = 0.3)
125–160	65	sulfuric	P4(η_{PAPR} = 0.7), P5(η_{PAPR} = 0.5), P6(η_{PAPR} = 0.3)
250–500	75	sulfuric	P7(η_{PAPR} = 0.7), P8(η_{PAPR} = 0.5), P9(η_{PAPR} = 0.3)
250–500	65	sulfuric	P10(η_{PAPR} = 0.7), P11(η_{PAPR} = 0.5), P12(η_{PAPR} = 0.3)
125–160	69	phosphoric	P13(η_{PAPR} = 0.7), P14(η_{PAPR} = 0.5), P15(η_{PAPR} = 0.3)
125–160	62	phosphoric	P16(η_{PAPR} = 0.7), P17(η_{PAPR} = 0.5), P18(η_{PAPR} = 0.3)
250–500	69	phosphoric	P19(η_{PAPR} = 0.7), P20(η_{PAPR} = 0.5), P21(η_{PAPR} = 0.3)
250–500	62	phosphoric	P22(η_{PAPR} = 0.7), P23(η_{PAPR} = 0.5), P24(η_{PAPR} = 0.3)
125–160	75	sulfuric	P29(η_{PAPR} = 1)
125–160	65	sulfuric	P30(η_{PAPR} = 1)
250–500	75	sulfuric	P31(η_{PAPR} = 1)
250– 500	65	sulfuric	P32(η_{PAPR} = 1)
125–160	69	phosphoric	P25(η_{PAPR} = 1)
125–160	62	phosphoric	P26(η_{PAPR} = 1)
250–500	69	phosphoric	P27(η_{PAPR} = 1)
250–500	62	phosphoric	P28(η_{PAPR} = 1)

In the picture from 1 to 8 changes in the phosphorus water soluble and 2 % citric acid soluble compounds in ratio to total phosphorus compounds content were presented.

Comparison of curves obtained for products with different raw material particle size (P13 Fig. 1 and P19 Fig. 2) and identical other parameters allows to conclude that the impact of raw material particle size is greater in the case of preparations obtained by using sulfuric acid. The reason of this phenomenon might be the formation of phosphogypsum in the first stage of the dissolution with sulfuric acid. As a result

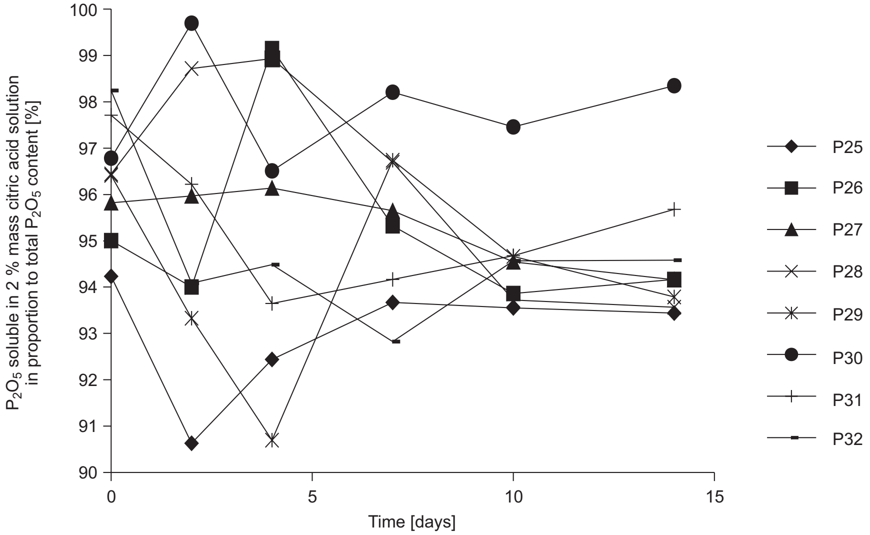

Fig. 1. Correlation P_2O_5 soluble in water in ratio to total P_2O_5 content in time for products from 1 to 8

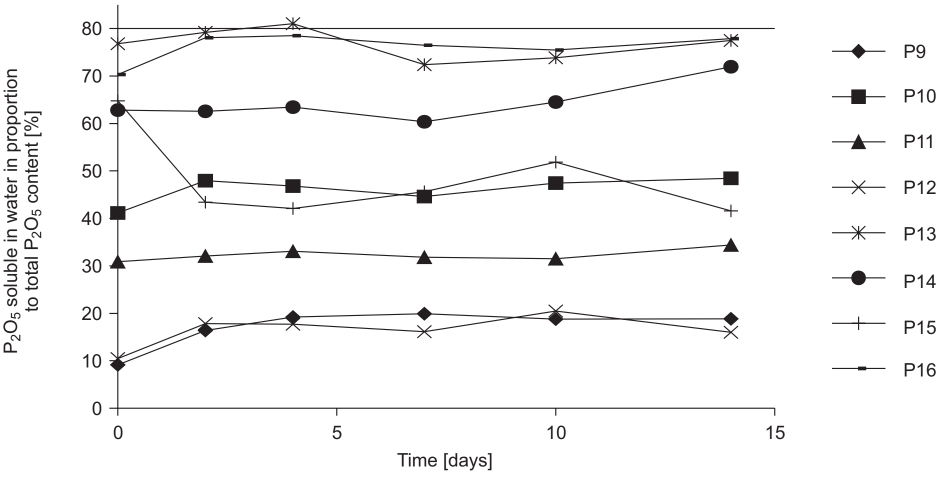

Fig. 2. Correlation P_2O_5 soluble in water in ratio to total P_2O_5 content in time for products from 9 to 16

phosphogypsum coats grains surface of raw material and stops further dissolution. In case of products which differ from each other by fineness and received on the basis of sulfuric acid it is clearly visible, that the differences in contents of various forms of phosphates are significant (P1 Fig. 1 and P10 Fig. 2). Influence of acid concentration on

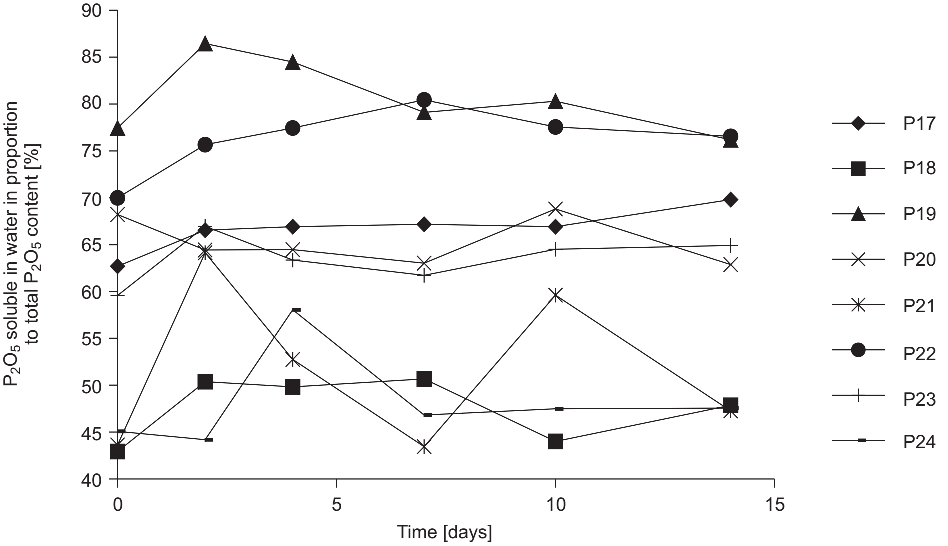

Fig. 3. Correlation P_2O_5 soluble in water in ratio to total P_2O_5 content in time for products from 17 to 24

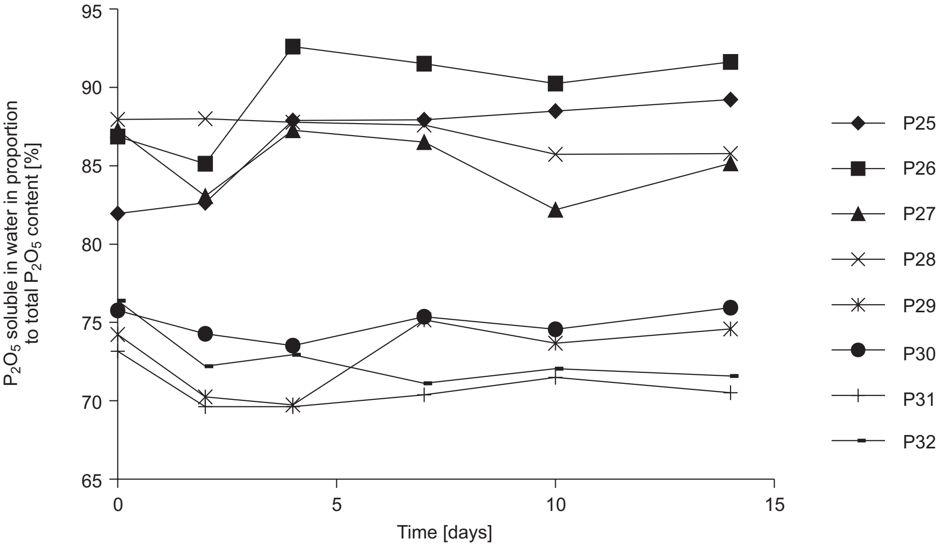

Fig. 4. Correlation P_2O_5 soluble in water in ratio to total P_2O_5 content in time for products from 25 to 32

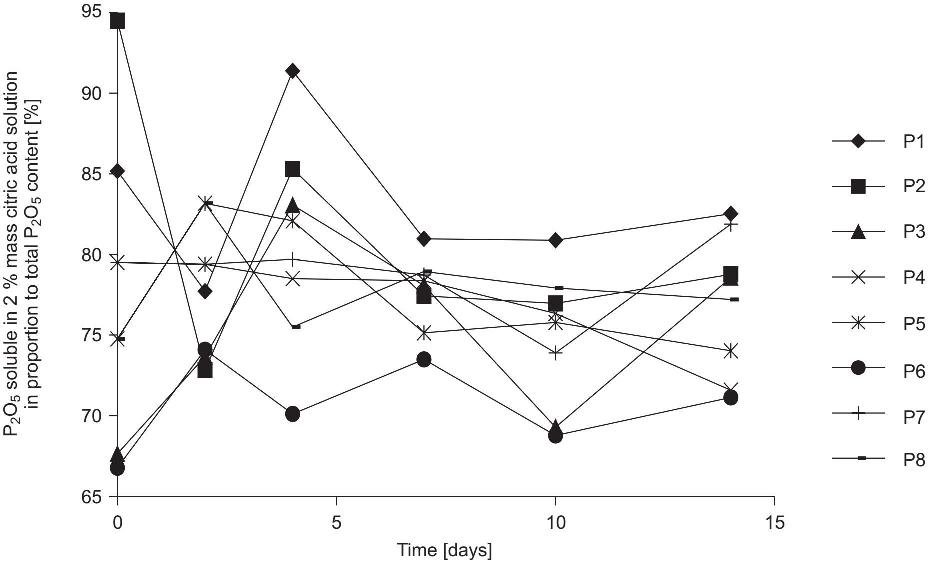

Fig. 5. Correlation P_2O_5 soluble in 2 % citric acid solution in ratio to total P_2O_5 content in time for products from 1 to 8

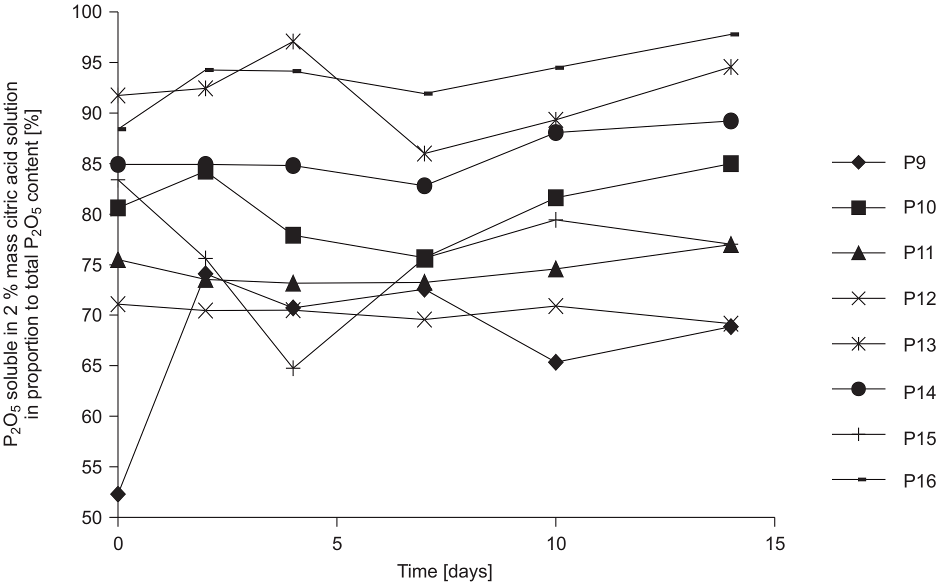

Fig. 6. Correlation P_2O_5 soluble in 2 % citric acid solution in ratio to total P_2O_5 content in time for products from 9 to 16

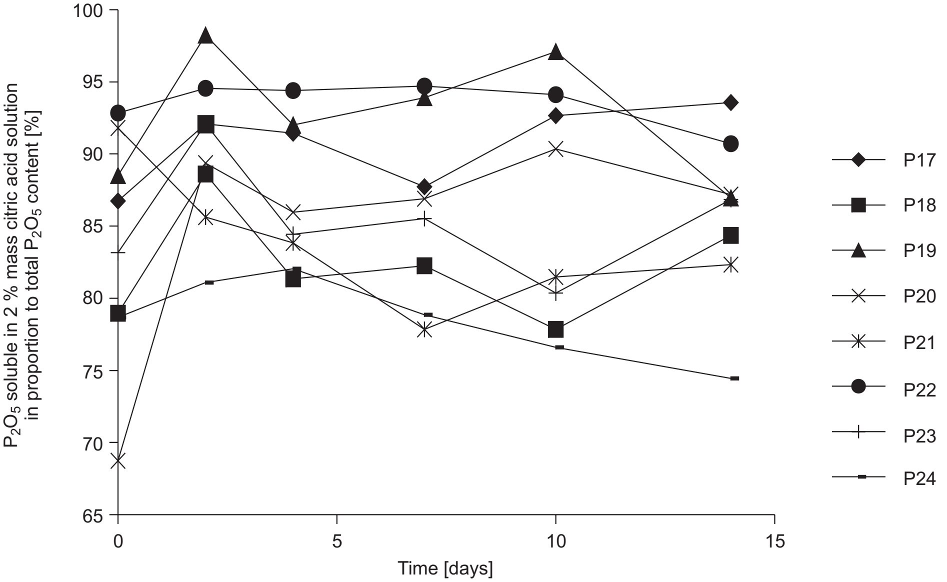

Fig. 7. Correlation P_2O_5 soluble in 2 % citric acid solution in ratio to total P_2O_5 content in time for products from 17 to 24

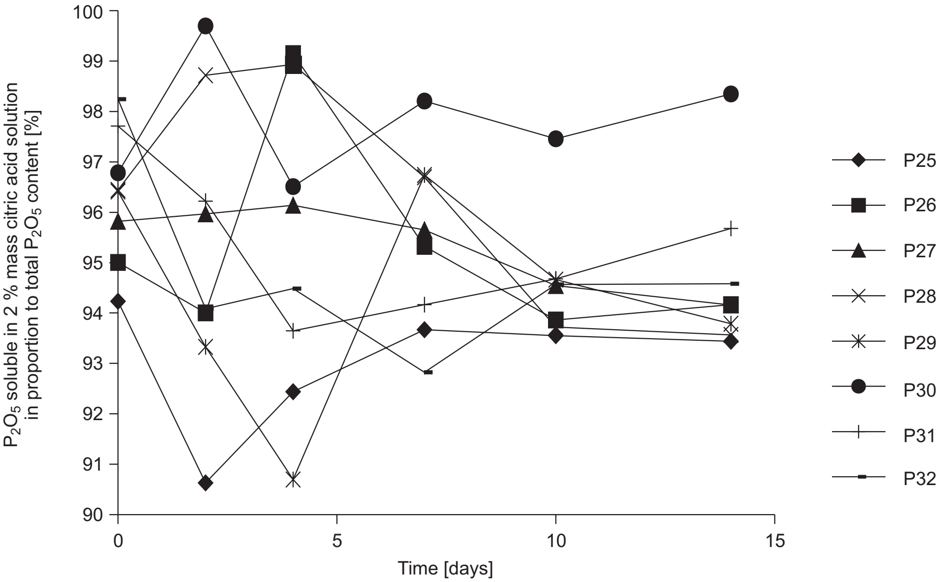

Fig. 8. Correlation P_2O_5 soluble in 2 % citric acid solution in ratio to total P_2O_5 content in time for products from 25 to 32

phosphorus compound content is minimal. Change of acid concentration in the range used during the trials, does not cause major changes in the content of individual forms of phosphates (P7 Fig. 1 and P10 Fig. 2).

Conclusions

1. PAPR type fertilizer samples manufactured by using phosphoric acid were specified by higher phosphates content (about 45 %) than manufactured with use of sulfuric acid.
2. Decrease in the acid amount used in the manufacture process caused decrease in the phosphorus content soluble in 2 % citric acid solution and in water, however drop in the water soluble phosphorus content is higher.
3. There was no significant influence of phosphate rock fineness on phosphates content in manufactured samples.
4. Small change in acid concentration (in the range used in industry) did not cause significant changes in phosphates content in samples.
5. When degree of PAPR stoichiometric norm (η_{PAPR}) was smaller *eg* 0.3–0.7 samples contained less moisture because water amount used in manufacture process was smaller than samples which were completely acidulated.
6. Samples manufactured with use of sulfuric acid contained more phosphates soluble in mineral acid than reference samples.
7. PAPR manufacture technology has few benefits from economical point of view, because it allows to reduce raw material and technological solution costs. It is important factor in fertilizer manufacturing based on phosphoric acid because it account for major raw material costs (even about 80 %). It is not so important in production of fertilizers based on sulfuric acid.

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BADANIA NAD CZĘŚCIOWYM ROZKŁADEM FOSFORYTU (METODĄ PAPR) Z ZASTOSOWANIEM KWASU SIARKOWEGO I FOSFOROWEGO

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Abstrakt: Przedstawiono wyniki badań nad wpływem różnych czynników przy częściowym rozkładzie surowca fosforowego na zawartość związków fosforu w produkcie nawozowym. Uwzględniono wpływ rodzaju, stężenia i ilości kwasu mineralnego oraz uziarnienia surowca na zawartość poszczególnych form fosforanów oznaczonych zgodnie z dyrektywą Unii Europejskiej (EC) No. 2003/2003 dotyczącą metod badań zawartości fosforanów w nawozach sztucznych.

Słowa kluczowe: fosforyty częściowo rozłożone (PAPR), kwasy mineralne, nawozy fosforowe, fosforany przyswajalne

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MIXTURES IDENTIFICATION OF CHEMICAL COMPOUNDS ON THE BASIS OF THEIR IR SPECTRA BY ARTIFICIAL INTELLIGENCE

IDENTYFIKACJA MIESZANIN ZWIĄZKÓW CHEMICZNYCH NA PODSTAWIE ICH WIDM W PODCZERWIENI Z WYKORZYSTANIEM SZTUCZNEJ INTELIGENCJI

Abstract: Infrared (IR) spectrometric identification of individual chemical compounds from their mixtures is still a challenging process. Therefore, we developed a method in which we use the IR "Fingerprint" spectra of a particular chemical substance followed by artificial intelligence (AI) – based analysis to correctly characterise components of relatively simple chemical mixtures. We describe here the assembly of tools developed especially for this purpose as well as the artificial neural network design together with the requirements that must be met for its proper functioning. To test our approach, we used a mixture of amphetamine and creatinine which are difficult to identify in mixtures by standard "Fingerprint" rules. The advantages of the artificial neural network approach include the generalisation and adaptation of knowledge by fitting parameter values to change the object characteristics. All this renders the effective identification of a mixture of two substances possible.

Keywords: chemical compounds, infrared spectroscopy, artificial intelligence, neural network

The traditional organic compounds identification method using IR absorption spectra (FTIR) is based on the identification of chemical functional groups contained within the molecules of tested compounds. We perform this by reading characteristic bands frequencies of a spectrum [1–4]. In the functional group identification we are using correlation tables which bind a frequency of a spectrum with a specific functional group. After determining the type of a functional group, compounds must be classified to appropriate chemical compounds class (to homologous series). The last stage of a

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compound identification is to find a spectrum in the IR spectrum catalog (in the identification of compound class section) with an identical image as the tested spectrum in the full intermediate IR range (4000; 400) cm^{-1}. The spectral identity of a compound is determined by searching for an identical spectrum in the catalog. This method is called *Fingerprint* (FP). The method is quite time-consuming and never gives a full guarantee of the identification accuracy.

For this reason, today, in the FP compounds identification method a suitable computer software is used to search the right compound in the spectral library. The library is located in the database and automatically determines the identity of a tested compound, specifying the spectral compatibility (sample – pattern) in a percentage.

Unfortunately, identification methods based on the FP are not applicable in the case of mixtures of two or more substances.

This paper presents an innovative method of identifying chemical compounds on the basis of their IR spectra, using the *artificial neural networks* (ANN) in a spectral analysis and a method for a quantitative analysis of binary mixtures. Due to the current demand, the analysis of binary systems using the ANN was conducted on the example of a creatinine and amphetamine mixture.

Identification method based on artificial neural network uses one of the main advantages of ANN – the possibility to generalise knowledge. This involves the identification of a chemical compound most similar to the one searched for in the database. In comparison with the FP, the methods of monosubstance and mixture identification using ANN have several advantages:

– In the FP method, the entire spectral ranges are compared with each other and the extent to which the overlap is checked, while the ANN compares the position and height of the top 20 maximum points.

– ANN is more sensitive to small spectral differences, therefore, it identifies substances in a mixture of compounds better than the FP method does; it is shown in this article on the example of mixtures of creatinine and amphetamines.

– ANN verifies the set of chemical functional groups in the substance, which gives more reliable results of identification.

– ANN "learns" finding the spectral differences between compounds, which is later used in the identification.

– ANN, even damaged, may continue to operate properly.

Artificial Neural Networks

ANN is a system performing certain calculations on the principle of simultaneous work of many interconnected elements (neurons). A similar structure has been observed in biological nervous system (ex. *human cerebellum*). It is composed of many neurons, which constitute a very simplified version of the original, and are much more easily combined with each other.

ANN was designed in such a way as to be convenient to track and easy to implement, which makes ANN have a flat and a set regular structure. Moreover, ANN should usually contain many neurons and should be able to work only as a whole.

The program described here uses ANN, whose neurons introduce corrections to their state of knowledge from the known values of the error committed. Output layer error is calculated from the difference of the expected and obtained value at the output of the network, while the error of neurons below the output layer is calculated by the back error propagation. A significant feature of this method is that its effect is independent of any theoretical assumptions. This means that the backward error propagation will always work [5–11].

Using the ANN for identification opens up new possibilities. Not only does it speed up the process, but also gives it the ability to adapt: to adjust the parameters to the changes of the characteristics of the object and to generalizes which means generating an appropriate response to the data not used in the learning process [12]. Also, ANN's ability to ignore redundant data and the data whose impact on the phenomenon is negligible has been used. Therefore, ANN focuses on the input data having a major impact for the modelled process. These are the crucial features which let ANN find application in many branches of science and technology [12–15].

ANN used in the program consists of:
– 20 entries,
– One hidden layer (consisting of 40 neurons),
– 10 outputs.

In order to identify the object, two neural networks were used: one to identify the number of wave bands, and the other with a maximum absorption of this bands.

A computer program for the diagnosis of chemical compounds based on the "fingerprint" of the infrared range using artificial neural networks

The program for the diagnosis of chemical compounds using ANN is written in C# and does not use any other tools to create an ANN such as Matlab. Figure 1 presents the

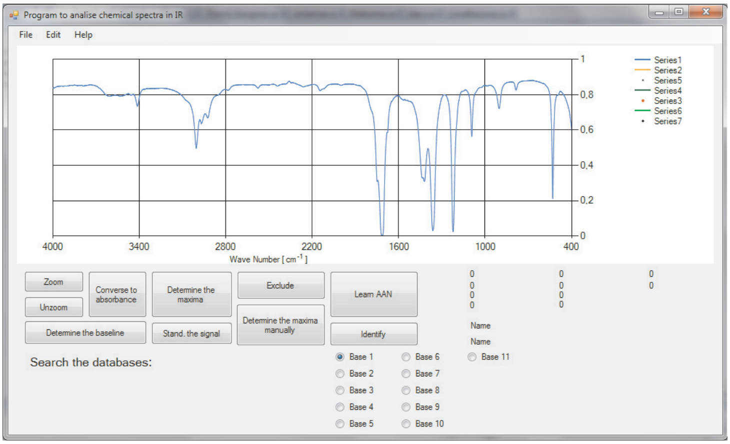


Fig. 1. General view of a computer program for the diagnosis of chemical compounds

main panel where the visible buttons are triggering processes responsible for the initial analysis of the test spectrum and for its further identification.

Before the spectrum is about to be subjected to a diagnosis, it should be examined first. The analysis involves determining transmission spectra and possibly replacing it with the absorption spectrum as well as designing the so-called base line (Fig. 2). The baseline is important because the values of the maximum individual bands are calculated from it and not from zero.

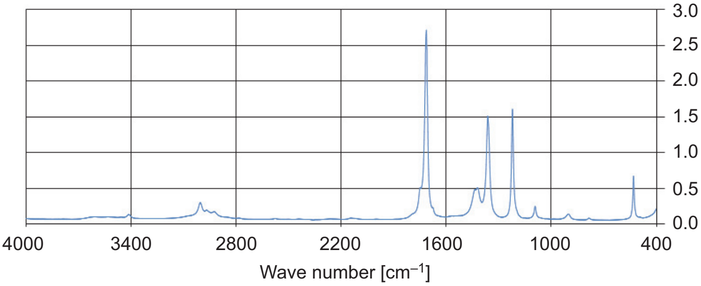


Fig. 2. Absorption spectra of acetone with a designated base line

After this process, the program determines the maximum points in each band (Fig. 3). This is done automatically using an algorithm written specially for this purpose and built into the program identifier. After determining the points, there are two possibilities of adjustment. The first concerns the selection of places where the program ignored the key points, while the second relates to the points that should not have been selected.

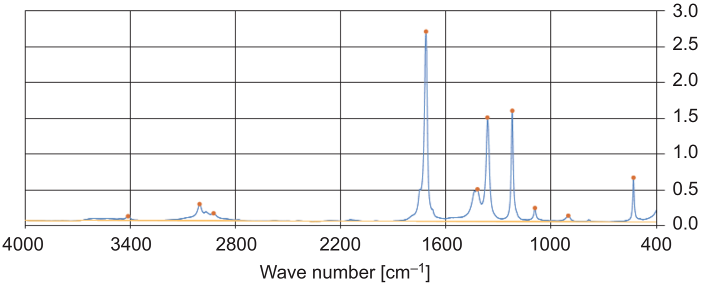
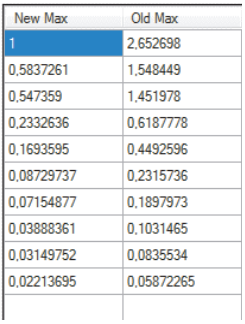


Fig. 3. Absorption spectra of acetone with designated points of maximum

The next process is the standardisation of the signal which will be then sent to the input ANN. The highest determined value of the absorption spectrum is reduced to unity, while lower values according to the principles of proportion to the respective values (Fig. 4). This solution increases the effectiveness of training an ANN, and thus the identification of chemical compounds. The substances may be present in different concentrations and peak heights of individual absorption bands may differ, even though



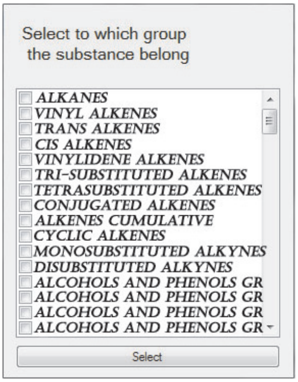
New Max	Old Max
1	2,652698
0,5837261	1,548449
0,547359	1,451978
0,2332636	0,6187778
0,1693595	0,4492596
0,08729737	0,2315736
0,07154877	0,1897973
0,03888361	0,1031465
0,03149752	0,0835534
0,02213695	0,05872265

Fig. 4. Standardisation of the input signal

they belong to the same compound. The introduction of standardised signal solves this problem, because all values are imported by the proportion of one value, and as the identification method theory says the substances have a fixed relationship of the individual absorption bands and this operation is therefore possible.

Before the program proceeds to the final stage of identification, it still has to designate of specific chemical functional groups, which the program executes automatically, too.

This is a part of the verification because the program checks whether the spectrum may belong to a given substance by checking the chemical functional groups (it may designate more than one group) with the group stored in the database. Figure 5 shows the window for selecting the chemical functional groups at the time of creating a database of compounds.



Select to which group
the substance belong

- ☐ ALKANES
- ☐ VINYL ALKENES
- ☐ TRANS ALKENES
- ☐ CIS ALKENES
- ☐ VINYLIDENE ALKENES
- ☐ TRI-SUBSTITUTED ALKENES
- ☐ TETRASUBSTITUTED ALKENES
- ☐ CONJUGATED ALKENES
- ☐ ALKENES CUMULATIVE
- ☐ CYCLIC ALKENES
- ☐ MONOSUBSTITUTED ALKYNES
- ☐ DISUBSTITUTED ALKYNES
- ☐ ALCOHOLS AND PHENOLS GR
- ☐ ALCOHOLS AND PHENOLS GR
- ☐ ALCOHOLS AND PHENOLS GR
- ☐ ALCOHOLS AND PHENOLS GR

Fig. 5. The choice of chemical functional groups

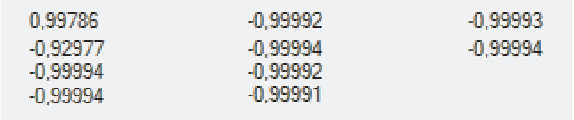
After determining the chemical functional groups, in the main panel there appears the information suggesting which database should be searched to find the chemical compound (Fig. 6). The displayed information is merely a hint and does not block the possibility of searching other databases.

Search the databases: 1, 2, 3, 4, 5, 6, 10, 11

● Base 1
○ Base 2
○ Base 3
○ Base 4
○ Base 5
○ Base 6
○ Base 7
○ Base 8
○ Base 9
○ Base 10
○ Base 11

Fig. 6. Designation database

The last stage of the program is the identification by ANN. It takes ANN quite a lot of time to learn, but the identification process itself takes a fraction of a second. ANN outputs are shown in Fig. 7; they are saved bitwise, so it is possible to write up to 1023 chemical compounds on them. Activation function that was used in the program is a bipolar function, so the program receives the output value of –1 and 1. The following figure has value of 1 in only the first position, which is the information to the program that the spectrum points are the first link in the database.



```
0,99786          -0,99992          -0,99993
-0,92977         -0,99994          -0,99994
-0,99994         -0,99992
-0,99994         -0,99991
```

Fig. 7. ANN outputs

Results and discussion

In order to confirm the effectiveness for the identification of chemical compounds methods based on their infrared spectra using the ANN, a study of mixture of two chemical compounds – creatinine and amphetamine – was performed. Figure 8 shows absorption spectrum of amphetamine, while the absorption spectrum of creatinine is in Fig. 9.

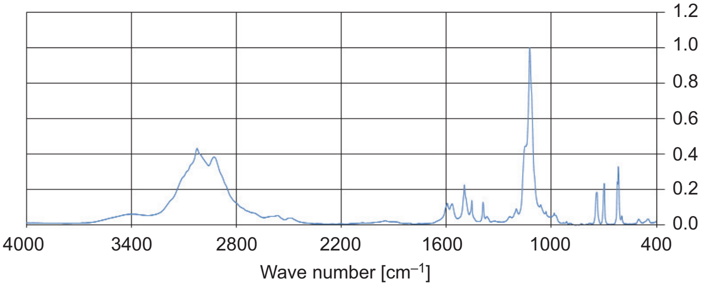


Fig. 8. The absorption spectrum of amphetamine

Because the samples were made using FTIR (Fourier Transform Infrared Spectroscopy), it is possible to mix them by the computer program. In this way, fourteen samples were created containing amphetamines from 5 % to 95 % in steps of 5 %.

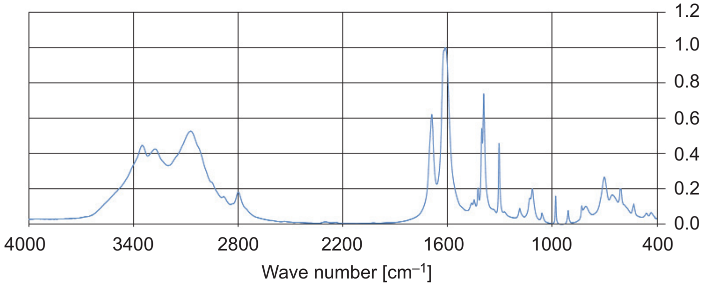


Fig. 9. The absorption spectrum of creatinine

Both spectra have characteristic bands in similar positions, and the additional difficulties is the fact that the band at the time of mixing the two substances overlap to themselves blurring the differences and make the mixture very difficult to identify later. Figure 10 shows the spectrum of the mixture of creatinine (40 %) and amphetamines (60 %).

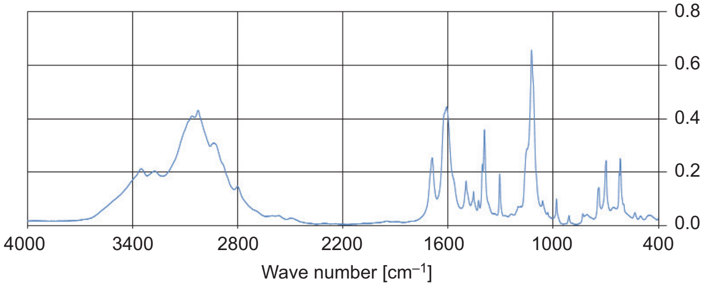


Fig. 10. Absorption spectrum of a mixture of creatinine (40 %) and amphetamines (60 %)

Figure 11 shows the same mixture, but in inverted proportions (creatinine – 60 %, amphetamines – 40 %). While in this case it is easy to discern the difference between the two spectra, it is far more difficult to notice the differences between the spectra of

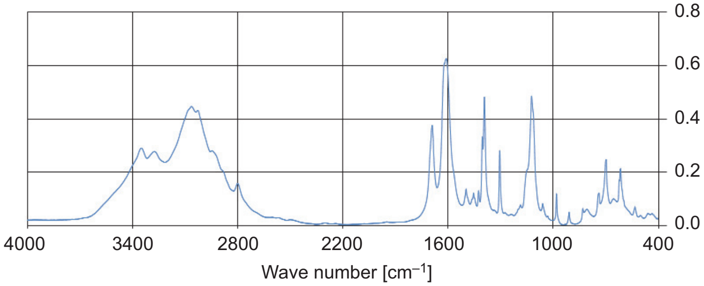


Fig. 11. Absorption spectrum of a mixture of creatinine (60 %) and amphetamines (40 %)

pure creatinine and the mixture having only 5 % of amphetamine, as it is shown in Fig. 12.

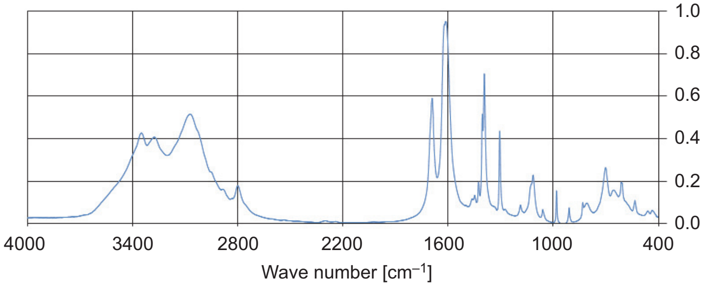


Fig. 12. Absorption spectrum of a mixture of creatinine (95 %) and amphetamines (5 %)

The database of 16 spectra was used by ANN to learn how to identify mixtures and compounds. ANN managed to find the minimum differences separating different spectra, and used this knowledge in their subsequent identification. After the learning process completed, ANN was able to recognise all of the 16 samples with a very high efficiency. In this case, ANN managed much better than the identification schemes used before, encountering problems only when there was less amphetamine than creatinine in a mixture.

Conclusions

Although the ANN has been known worldwide for nearly 50 years, its potential has still not been fully exploited. There are many areas of science and technology, where it will certainly find wider use, as it is the case with the identification of chemical compounds based on their infrared spectra. Software developed for this purpose can be a useful tool for rapid diagnosis of substance, for example in forensic laboratories. The presented method certainly needs improvement, but the results show that it is an effective and reliable method of identification.

Acknowledgement

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NARODOWA STRATEGIA SPÓJNOŚCI

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IDENTYFIKACJA MIESZANIN ZWIĄZKÓW CHEMICZNYCH NA PODSTAWIE ICH WIDM W PODCZERWIENI Z WYKORZYSTANIEM SZTUCZNEJ INTELIGENCJI

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Abstrakt: W artykule przedstawiono możliwości zastosowania w identyfikacji związków chemicznych metody tzw. odcisku palca oraz sztucznej inteligencji na podstawie widm w podczerwieni. Opisano budowę opracowanego specjalnie do tego celu narzędzia i sztuczną sieć neuronową oraz wymogi, jakie muszą być spełnione do jej poprawnego funkcjonowania. Obecnie stosowane programy użytkowe do identyfikacji związków chemicznych na podstawie ich widm w podczerwieni natrafiają na trudności z poprawną identyfikacją w przypadku mieszanin substancji. W przeprowadzonych badaniach testowych wykorzystano mieszaninę kreatyniny oraz amfetaminy – substancje z którymi obecnie wykorzystywane oprogramowania działające wg zasady Finger-print mają duże trudności. Dlatego też zastosowano sztuczną sieć neuronową, której zalety, takie jak uogólnianie zdobytej wiedzy oraz adaptacja, czyli dopasowania wartości parametrów do zmian charakterystyk obiektu, pozwalają na skuteczną identyfikację w mieszaninie dwóch substancji.

Słowa kluczowe: związki chemiczne, podczerwień, spektroskopia, sztuczna inteligencja, sieć neuronowa.

Varia

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