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CONTENTS

VARIA

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VARIA

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Małgorzata RAJFUR[1]

ALGAE AS A SOURCE OF INFORMATION ON SURFACE WATERS CONTAMINATION WITH HEAVY METALS

GLONY JAKO ŹRÓDŁO INFORMACJI O ZANIECZYSZCZENIU METALAMI CIĘŻKIMI WÓD POWIERZCHNIOWYCH

Abstract: This paper is a synthetic set of information that relate to the goals and directions of research linked with the use of algae for the assessment of contamination of surface water by heavy metals. The presented examples concern the use of algae in biomonitoring of aquatic ecosystems, which in many countries, including Poland became a permanent part of an integrated environmental monitoring. The paper discuss the results of research carried out in situ, whose aim was to assess the contamination of selected aquatic ecosystems by heavy metals based on the chemical composition of thalluses, as well as the identification of potential sources of these analytes. The analysis of the research results referred to in the cited literature was supported by the conclusions of the research of their own.

Keywords: algae, heavy metals, surface waters, biomonitoring

The term *algae* (Gr. *Phykos,* Lat. *Algae*) is used to refer to a group of thallus plants, *ie* paraoza (morphological groups: *Protophyta* and *Thallophyta*). Among them, apart from eukaryotes (inter alia *Spirogyra* sp.), there are also organisms with prokaryotic cell structure, such as blue-green algae (*eg Nostoc commune*), also known as *Cyanobacteria*. The author of one of the pioneering works devoted entirely to this group of organisms is Samuel Gottlieb Gmelin (1744–1774). In his work *Historia Fucorum* (*fucus* – the term used to describe algae, introduced by the Romans and commonly used till the end of the 18th century), published in 1768, he described 99 species of algae. Many of the algae species described by Gmelin have disappeared by now. At present, the term *algae* covers over 27 thousands of species in various systematic groups of thallus plants [1]. In Poland, the term was introduced into the botanical terminology by Jozef Rostafinski (1850–1928) [2–5].

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Algae do not constitute a systematic unit; however, due to practical reasons, a certain taxonomic order was introduced, which is manifested, depending on the interpretations of individual authors, by a creation of some systems. Since 1931, the system of Adolf Pascher had been used, according to which the algae were divided into 9 phyla: *Cyanophyta*, *Glaucophyta*, *Euglenophyta*, *Pyrrophyta*, *Chrysophyta*, *Chlorophyta*, *Charophyta*, *Phaeophyta* and *Rhodophyta* [6]. Taxons differentiated in 1980 by H. Ettl are based on this system. Algae were divided into 9 phyla, and the tenth phylum, conditionally included to algae, consists of *Cyanophyta* [4]. In 1995, Christiaan van den Hoek introduced a new taxonomy of algae, differentiating 11 phyla [7, 8]. Among them, there are two prokaryotic phyla: blue-green algae (*Cyanophyta* = *Cyanobacteria*) and *Prochlorophyta*, as well as 9 eukaryotic phyla: glaucophytes (*Glaucophyta*), haptophytes (*Haptophyta*), cryptophytes (*Cryptophyta*), dinophytes (*Dinophyta*), euglenoids (*Euglenophyta*), red algae (*Rhodophyta*), yellow-green algae (*Heterokontophyta*), chlorarachniophytes (*Chlorarachniophyta*) and green algae (*Chlorophyta*) [9]. In 2000, James E. Graham and Lee W. Wiloox introduced the term "classification of blue-green algae and algae", which covered the orders and classes, but without differentiation into phyla [8, 10].

Algae are encountered in every place where water is present, at least periodically. They inhabit both the aqueous environment and land. They live both in saltwater (saline, salty lakes, seas and oceans) and in freshwater (springs, rivers, ponds, lakes and swamps). Some species are able to live on snow and ice, while others in hot springs (the highest temperature at which algae were found was 358.2 K). Due to different ecological requirements, algae can be divided into 11 groups. Table 1 shows the ecological groups of algae, their brief characteristics as well as some examples of algae species [4].

Algae display varied morphological structure of the thallus (single-celled species (*Ochromonas ludibunda*), species forming colonies (*Hydrurus foetidus*), and multi-celled organisms (*Ulva lactuca*), species with thread-like thallus (*Cladophora*) and ramified thallus (*Caulerpa prolifera*). They also vary in shape and size, from species as small as 1 μm to large, leaf-like species that fix to surfaces using rhizoids (thread-like processes). In the trophic chain, algae are mostly autotrophic, although heterotrophic algae and algae that enter symbiotic relations with other organisms are also encountered. For instance, the symbiotic relations between algae and fungi take the form of lichens [4, 5, 11, 12].

Studies carried out on algae concentrate on, among others, their chemical composition, biology, taxonomy, physiography and also their application for the assessment of water contamination with heavy metals, pesticides and radionuclides.

The main research issues realised in the process of aqueous ecosystems biomonitoring with the application of algae include the following: the assessment of contamination of the studied aqueous reservoirs (both saltwater and freshwater reservoirs), identification of contamination sources, a long-term monitoring and assessment of tendencies in changes in the chemical composition of contamination, as well as comparative studies.

Table 1

Classification of algae due to their ecological requirements [4]

Ecological group	Characteristics of ecological conditions	Algae species
Planktonic algae	Algae suspended in water and passively drifting with water currents	*Triposolenia longicornis*
Neuston	Algae living on the border of water and atmosphere (the surface film of a body of water)	*Chromulina rosanoffii*
Benhtos	Algae living on the bottom or the bank of water reservoirs	*Chaetomorpha aerea*
Algae of inland salty waters	Algae existing in saline and salty lakes; salinity level may be 60–80 ‰	*Dunaliella salina*
Algae on snow and ice	Algae existing on the surface of snow and ice; defined as cryophytes, cryoplankton, cryoseston,	*Chlamydomonas nivalis*
Hot springs algae	Algae existing in hot springs (thermal springs)	phylum *Chrysophyta*
Soil algae	Algae existing in the surface layer of soil (up to several dozen cm)	*Chlorhormidium flaccidum*
Terrestrial algae	Algae existing on a damp surface of soil; defined as geophytes	*Botrydium granulatum*
Aerophytic algae	Algae existing in places periodically damp, *eg* building roofs, walls, rocks	*Trentepohlia iolithus*
Epibiontic algae	Algae existing on the surface of living organisms – plants and animals	*Chlorangiopsis epizoica*
Algae in a living environment	Algae existing on another living organism (symbiosis, parasitism)	*Schmitziella endophloea*

Aqueous ecosystems are sensitive to physicochemical changes in biotope. In order to monitor some of these changes, such as heavy metal concentration, the bioindicators and biomonitors are applied, *ie* organisms which indicate the measurable morphological, anatomic and physiological changes [13]. These organisms, in order to be used as effective indicators of environmental pollution level, must fulfil certain criteria, for instance such as the following: relatively sedentary lifestyle, wide geographical prevalence, easiness to identify and sample, relatively high tolerance in relation to the studied pollution and the existence of statistically significant correlation between the analyte concentration, *eg* in water and in the organism that lives in this water [14]. Algae, due to their abundance in highly diversified environmental conditions, are becoming more and more popular biomonitors [15]. Additionally, they are very good sorbents of heavy metals. The author's own studies led to the conclusion that a sample of the alga *Parmalia palmata* with the mass of 1.0 g, after being placed in the 400 cm^3 of $CdCl_2$ solution with concentration of 0.5 mg/dm^3 accumulates almost 100 % of Cd^{2+} ions present in this solution.

The aim of this paper is to collect and systematise data regarding assumptions and trends in the studies carried out on different species and types of algae. The paper presents information regarding biomonitoring studies connected with the assessment of contamination levels of aqueous ecosystems with heavy metals on the basis of the analysis of thallus chemical composition of algae. Some practical applications of algae are suggested, for instance in water phytoremediation and in the process of sewage treatment.

Biomonitoring of freshwater ecosystems

There is a high diversity in freshwater ecosystems in nature. Small reservoirs, rock or ground hollows filled with water belong to periodical waters. Bigger reservoirs (ponds and lakes), as well as flowing waters (springs, brooks and rivers) belong to more or less permanent waters. The character of such ecosystems changes significantly depending on their morphometry as well as the type of catchment basin [11]. Numerous biomonitoring studies of the freshwater ecosystems have been carried out, in which the indicator organisms are algae. One of the examples is the study utilising algae such as *Spirogyra adnata* to determine the contamination of the waters of lake Naintial, situated at the foot of the Himalayas (India) with metals: Cr, Cu, Fe, Mn, Ni, Pb and Zn. As compared to other species of the same phylum *Chlorophyta, eg Oedogonium* sp., thalli of *Spirogyra adnata* contained large concentration of Pb (95 μg/g d.m.). Heavy metals in algae were determined by the atomic absorption spectrometry method (AAS). Potential sources of heavy metal contamination of this reservoir include the following: tourism development on the studied area, commuter traffic and illegal construction works. The authors concluded that algae, due to their very good sorption properties, may be applied in phytoremediation, *eg* to remove heavy metals from water [16]. This conclusion is confirmed by the results published in literature [17–19].

In India, the biomonitoring studies were carried out on lake Pulicat (South-Eastern India). By means of the AAS method, the following heavy metals were determined in the alga *Ulva lactuca*: Cd, Cr and Pb. Concentrations of metals accumulated in algae were compared with the concentrations in benthic sediments and the water of the lake. It was observed that in the alga *Ulva lactuca* and in the sediments, heavy metal concentrations were changing in accordance with the column: Cr > Pb > Cd, while in water the most abundant metal was Cr and the least abundant was Pb. The authors also observed seasonal changes in Cd and Pb concentration in the algae and sediment samples [20].

From April 2000 to December 2004, the contamination with such metals as Cd, Cr, Hg and Pb was monitored in the water of lake Sariyar in Turkey. Samples of water and phytoplankton containing algae of the phyla *Chlorophyta*, *Chrysophyta*, *Euglenophyta* and others were used for the study. Seasonal changes in concentrations of Cd, Cr, Hg and Pb were observed (determined by means of the AAS method) in the samples of water and phytoplankton. Significantly higher concentrations of some of the analysed metals were observed in phytoplankton (the heavy metal concentrations were changing in accordance with the column Pb > Cr > Cd > Hg) as compared with the water samples. For instance, Cd concentration in water, in summer, was app. 20 mg/dm^3 and in phytoplankton app. 75 mg/g, while in winter, in water the concentration was app 35 mg/dm^3, and in phytoplankton app. 105 mg/g. It was observed that the differences in heavy metal bioaccumulation result from the seasonal variability of algae species in phytoplankton, as well as different sorption properties of various algae species [21].

In Turkey, the biomonitoring studies of the Tigris River were carried out. On the basis of heavy metal concentrations (determined by means of the AAS method): Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn, accumulated by the algae *Spirogyra* sp., the assessment of contamination of the studied ecosystem was conducted. It was observed that heavy -

metal concentrations in algae undergo seasonal changes. The highest concentrations: Co, Cu and Ni were determined in summer, Mn and Fe in autumn and Zn in spring [22].

From January 1992, water and algae collected from two streams near the city of Shillong in India were analysed: Wah Diengling, flowing through forested areas (the outskirts of the city) and Umkhrah, flowing through highly urban part of the city of Shillong. By means of the AAS method, the following heavy metals were determined: Cd, Cu, Mn, Pb and Zn. It was observed that the algae collected from the stream Umkhrah revealed app. twice higher Pb concentration, three-fold higher Zn concentration and five-fold higher concentration of Cd, Cu and Mn as compared to the algae samples collected from the stream Wah Diengling. It was shown that high heavy metal concentration in algae from the stream Umkhrah resulted from its localisation. This watercourse was fed with sewage from nearby shops, garages, households, as well as water coming from arable fields (crop protection chemicals contain high concentrations of Cu and Mn) [23].

Other examples of biomonitoring studies of freshwater ecosystems with the utilisation of algae are studies carried out in Poland (the Large Turawa Lake, the Odra River) [24, 25], the Czech Republic (the Thaya River) [26], Russia (12 rivers of the Kola Peninsula, The Yenisei River in Siberia, Lake Baikal) [27–29], Scotland (a lake in the range of the Lochnagar Mountains) [30], Greece (the Evros River delta) [31], Argentina (lakes in the Andes: Nahuel Huapi, Gutirrez and Moscardi) [32], Uganda (Lake George, a brook near the city of Kampala) [33, 34], Nigeria (the Niger River) [35], Malawi (watercourses near the city of Blantyre, Eastern Africa) [36], The USA (a watercourse near the city of Oak Ridge, the Missouri River) [37, 38]. Australia (4 rivers near Sydney: Hawkesbury, Parramatta, Cooks and Clyde) [39].

Literature data confirms that algae sorb heavy metals under natural conditions. Biomass collected from waters with high concentrations of heavy metals is characterised by higher concentrations of these analytes in their structures as compared with the biomass collected from uncontaminated waters. The authors indicate that algae are highly sensitive biosensors, sensitive to, for instance, seasonal changes in analyte concentrations in aqueous ecosystems. A correlation between heavy metal concentration in algae and in benthic sediments and water has still been investigated.

Biomonitoring of saltwater ecosystems

Saltwater ecosystems, due to their diversified physical environment (biotope), are also characterised by a high diversification of biocenoses. There are various categories of saltwater ecosystems. These include ecosystems of tide zone, littoral zone, offing and ocean depths. Also in the case of these ecosystems, various biomonitoring studies with algae have been carried out for many years. As an example, the studies in the Gulf of Aden (Yemen) can be quoted, in which the algae of phyla *Chlorophyta*, *Phaeophyta* and *Rhodophyta* were used. It was observed that concentrations of heavy metals accumulated in algae were several orders of magnitude higher than in water, while the highest heavy metal concentrations were found in the *Chlorophyta* phylum. It was also shown that algae, depending on their species, accumulated some metals selectively [40].

Another example in this field of research is the study in the Black Sea, The Bosphorus, and the Sea of Marmara. Heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were determined in the samples of benthic sediments, algae and fish. It was observed that during the experiment, between 1998 and 2000, the contamination level of the analysed water reservoirs with these analytes decreased [41].

In the Thermaikos Gulf (Greece), the accumulation of heavy metals (Cd, Cu, Fe, Pb and Zn) in the alga *Ulva rigida* and in benthic sediments was assessed. The samples were collected along the gulf coastline. Seasonal changes in the concentration of the analysed analytes in algae was observed, connected, for instance, with a different dynamics of biomass growth, depending on the season. The authors indicated positive correlations in concentrations of Pb and Cu, Fe and Cu as well as Cd and Pb determined in algae and benthic sediments. The concentration of the analysed analytes in water and in algae was decreasing in accordance with the column Fe > Zn > Pb > Cu > Cd. On the basis of the conducted studies the authors concluded that the alga *Ulva rigida* may be good biomonitors of aqueous environment contamination with metals: Pb, Zn and Cd [42, 43]. In the biomonitoring studies in the Gulf of Thermaikos the algae *Gracilaria verrucosa* [44] and *Enteromorpha linza* [45] were also used.

On the basis of the literature review presented above, the author of this paper marked on the map in Fig. 1 the saltwater ecosystems covered with biomonitoring in which different species of algae were used.

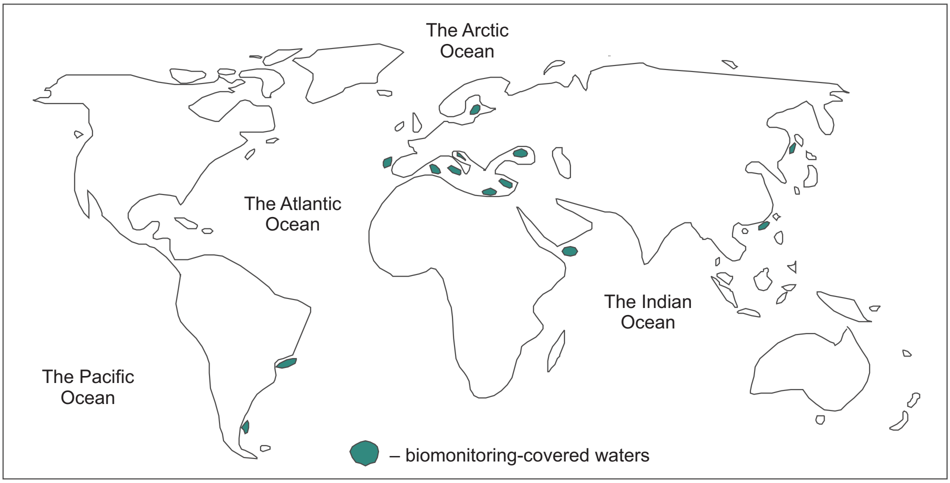

Fig. 1. Oceanic and sea waters covered with biomonitoring with algae

Biomonitoring studies with the application of algae were also conducted in Poland (the Baltic Sea) [46, 47], Russia (the Sea of Japan) [48], China (the waters of the South China Sea at the coast of Hong Kong were monitored) [49, 50], Portugal (the waters of the Ria de Aveiro lagoon) [51], Italy (the Mediterranean Sea, the Tyrrhenian Sea, the Adriatic Sea) [52–54], Bulgaria (the Black Sea) [55, 56], Greece (the Aegean Sea) [57], Algeria (the Mediterranean Sea) [58], Egypt (the Mediterranean Sea) [59], Turkey (the

Black Sea, the eastern coast of the Aegean Sea, the Marmara Sea) [60–62], Brazil (the waters of Sepetiba Bay, Guanabara Bay, Ribeira Bay and the Gulf of San Jorge were monitored) [63–67].

Literature analysis regarding the biomonitoring of saltwater ecosystems confirmed that algae may be used as bioindicators. On the basis of the analysis of chemical composition of thalli, it can be determined whether a given water reservoir is contaminated with a specific analyte. However, there is no reliable method, the application of which could facilitate the assessment of contamination of a given reservoir with heavy metals through the analysis of these metals concentrations in algae samples.

Aqueous ecosystems contamination with heavy metals – analytes bioaccumulation in situ

The algae, which live in aqueous ecosystems, that are diversified in terms if physico-chemical parameters, are characterised by various concentrations of heavy metals in thalli. Table 2 presents average concentrations of heavy metals in thalli collected from different aqueous ecosystems.

Table 2

Heavy metal concentrations in algae living in different ecosystems [μg/g d.m.]

Mn	Fe	Cu	Zn	Cd	Pb	Alga	Location	Ref.
176	115	47	34	—	95	*Spirogyra adnata*	the Nainital Lake, India	[16]
—	—	—	—	38.1	11.6	*Ulva lactuca*	the Pulicat Lake, South East India	[20]
106.4	—	22.7	38.3	0.21	14.3	Algae	the Way Diengling stream	[23]
658.0	—	113.1	109.2	1.16	26.0	Algae	the Umkhrah stream	[23]
45.1	778	13.8	21.2	< 0.02	< 0.1	*Ulva lactuca*	the Black Sea – the Sile station	[41]
41.1	902	11.3	13.5	< 0.02	< 0.1	*Ulva lactuca*	the Black Sea – the Sinop station	[41]
192.4	8821	18.2	43.2	< 0.02	< 0.1	*Enteromorpha linza*	the Black Sea – the Sile station	[41]
778.4	616.1	9.4	16.9	0.22	1.1	*Fucus vesiculosus*	the North Sea – Holy Island, England	[68]
105.2	2197	29.1	286.4	1.10	15.4	*Ulva lactuca*	the Marmara Sea – the Menekşe	[62]
—	4149	74.1	5.0	—	93.5	*Ulva lactuca*	the Tolo Harbour, Hong Kong	[69]

Concentrations of heavy metals accumulated in algae *in situ* depend, for instance, on the characteristic (different, frequently changeable) contamination of waters and benthic sediments with heavy metals, their bioaccessibility for the elements of biota, algae sorption properties and the concentration of other, outside analytes in the aqueous reservoir.

In order to assess the bioaccumulation capacity of heavy metals by the biota elements, *eg* algae, a bioconcentration factor (*BCF*) is determined [70].

$$BCF = c_{x,a} / c_{x,w} \tag{1}$$

where: x – heavy metal ions,
$c_{x,a}$ – heavy metal concentration in algae [mg/kg d.m.],
$c_{x,w}$ – heavy metal concentration dissolved in water collected from the site of algae sample collection [mg/dm^3].

The values of the factor *BCF* > 1000 reveal very good sorption properties of the biota elements (*eg* the aqueous plants: *Hydrocotyle umbellata* [71] and *Eichhornia crassipes* [102], zooplankton [70, 73], and algae [74]), and suggest the possibility of their application in biomonitoring and effective phytoremediation [71]. Table 3 shows the values of the *BCF* factor showing the accumulative properties of the analysed species of algae in relation to the analysed heavy metals.

Table 3

Values of the bioconcentration factor (*BCF*)

Mn	Fe	Ni	Cu	Zn	Cd	Pb	Ref.
Spirogyra sp.							
12590	9090	2568	> 4200	12531	> 1527	> 1372	[75]
Enteromorpha sp.							
—	—	—	2833	—	1125	4423	[76]
Bostrychia sp.							
90000	$> 18 \cdot 10^6$	5555	47778	93810	—	$> 7 \cdot 10^5$	[39]
Caloglossa leprieurii							
20000	$> 1 \cdot 10^7$	4444	37778	76429	—	$> 3 \cdot 10^5$	[39]

The determination of the values of bioconcentration factors reveals very good sorption properties of the analysed algae. A varied bioaccessibility of the determined heavy metals in relation to the algae thalli may be influenced by, for instance, the form of analyte existence, concentration and the time of exposure of a plant to its activity, cellular distribution of metal, forms of storing and detoxication of metal, interactions with other compounds present in the cell and the specific features (*eg* adaptive capacity) [77].

In order to assess the contamination of waters with heavy metals, the algae are used as biosensors in the passive biomonitoring (the analysis of the composition of algae naturally existing in the aqueous ecosystem). However, there are also studies within the active biomonitoring (transplanting/moving the algae from waters or cultures poorly contaminated with heavy metals to the ecosystems contaminated with the analyes). In France, the waters of the New Caledonia lagoon were studied. The algae *Lobophora variegata* were transplanted from waters with poor heavy metal contamination (the Maa Bay), with the concentration, *eg*, Cr < 0.02 μg/g d.m. to the waters contaminated with mining sewage (the Boulari Bay). In the three-month transplantation period, an increase in the analyte concentration in thalli was observed. Chrome concentration increased to app. 200 μg/g d.m. Transplantation of algae from the Boulari Bay to the area of the Maa Bay did not lead to a statistically significant desorption of analytes from the algae samples [78].

The authors of the publications on biomonitoring of aqueous ecosystems with the application of algae very rarely provide the assessment of uncertainty of the applied measurement methods. On the basis of the studies carried out by the author of this paper regarding the assessment of heavy metal contamination of the Large Turawa Lake (the south-western Poland), it was observed that the biomonitoring results may contain up to 26 % of the measurement uncertainty. For the samples of the alga *Spirogyra* sp. collected from three measurement sites of the studied reservoir, the value of the coefficient of variation CV_{mean} determined on the basis of the standard deviation value ranged between 20–26 %. The SD value differences for the samples collected from the same site result from heterogeneity of the studied material [25].

Summary and conclusions

Biomonitoring is gaining popularity as a method for assessing the pollution of various ecosystems, including the aquatic environments. It has the fundamental advantages of the inexpensive and straightforward sampling method which does not require any special personnel training, and of the natural ability of biomonitors to accumulate the accessible forms of pollutants. The analysis of concentrations of trace elements bound in thalli provides information regarding the pollutants introduced to the aqueous ecosystems. Studies with algae indicate a possibility of their application in the assessment of aqueous ecosystems contamination with heavy metals, in identification of contamination sources and in the long-term monitoring of the contamination level of the studied reservoirs. For the biomonitoring purposes the following algae are most frequently used: unicellular algae constituting phytoplankton and multicellular organisms, *eg Spirogyra adnata*, *Spirogyra species*, *Palmaria palmata*, *Ulva lactuca* and *Ulva rigida*. Whether a given species of algae can be used for water biomonitoring depends on its prevalence, which allows for collection of adequate amount of material. Also, in order to fulfil the requirement of representation in relation to the studied ecosystem, a given species of algae should manifest a relatively sedentary lifestyle.

One of the problems connected with biomonitoring is the validation of research procedures, which results from the multidimensionality of the algae-environment interactions. The sorption mechanisms and dynamic equilibria in the system algae-solution, including contamination bioaccumulation time have not yet been recognised sufficiently. Determining correlations between analyte concentrations in algae and in water, as well as identification of the abiotic factors influencing sorption may in the future be used for the purpose of a simple measurement of heavy metal concentrations in surface waters, which may be helpful in the development of a classification method of surface waters in which the algae will play the role of water quality biosensors.

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GLONY JAKO ŹRÓDŁO INFORMACJI O ZANIECZYSZCZENIU METALAMI CIĘŻKIMI WÓD POWIERZCHNIOWYCH

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Abstrakt: Publikacja jest syntetycznym zbiorem informacji, które dotyczą celów i kierunków badań związanych z wykorzystaniem glonów do oceny zanieczyszczenia wód powierzchniowych metalami ciężkimi. Zaprezentowane przykłady dotyczą wykorzystania glonów w biomonitoringu ekosystemów wodnych, który w wielu krajach, także w Polsce stał się trwałym elementem zintegrowanego monitoringu środowiskowego. Omówiono wyniki badań prowadzonych *in situ*, których celem była ocena zanieczyszczenia wybranych ekosystemów wodnych metalami ciężkimi na podstawie składu chemicznego plech, a także wskazanie potencjalnych źródeł tych analitów. Analizę wyników badań omówionych w cytowanej literaturze poparto wnioskami z badań własnych.

Słowa kluczowe: glony, metale ciężkie, wody powierzchniowe, biomonitoring

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IRON ACCUMULATION IN SELECTED ELEMENTS OF POND ECOSYSTEM FOOD CHAIN

AKUMULACJA ŻELAZA W WYBRANYCH ELEMENTACH ŁAŃCUCHA POKARMOWEGO EKOSYSTEMU STAWOWEGO

Abstract: The aim of this study was to determine the accumulation of iron in the individual links of aquatic ecosystems food chain under extensive farming of carp. Based on ascertained in these organisms the contents of this element calculated value of bioaccumulation in the aquatic system and evaluated the degree of contamination. The study was performed in the breeding pond, located in Mydlniki, supplied with water from the river Rudawa. From the study pond collected: water, sediment from the bottom of the pond, benthic organisms represented by the larvae of flies of the chironomid family organs in, and carps from which were dissected the most associated with metals metabolism organs (gills, gonads, liver and muscle). In all samples determine the content of iron by atomic emission spectrometry in the camera JY 238 Ultrace Jobin Yvon Emission. Digestion of the samples were made by the wet method in a closed system with the use of microwave energy. Based on the results concluded that in the studied ecosystem, there is no risk of iron poisoning. The contents of this element in the water and bottom sediments are comparable to other reservoirs, of anthropogenic and natural origin. Was found a high value of the sediments enrichment factor sediments with iron in relation to its content in the water. The content of iron in the benthic organisms have taken high values, from 1189 to 1997 mg $\cdot$ kg^{-1} d.m. The iron content in organisms of the examined fish ranged from 2.951 to 395.9 mg $\cdot$ kg^{-1} d.m. Most of this element was found in the gills, then in liver, gonads and the least iron is accumulated muscles. Literature data show that regardless of the amount of iron in the environment, bioaccumulation factor in fish organs takes a value close to those obtained in own research. The content of iron in the liver and gills of fish is the most authoritative indicator of environmental contamination by iron compounds.

Keywords: iron, bioaccumulation, food chain, aquaculture, carp

Intruduction

Comprehensive determining the extent of hazard to aquatic system posed by trace elements is very difficult due to considerable changeability of water and bottom

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sediments chemistry in the reservoir in time and spatial approach. Chemical elements supplied to the aquatic environment from anthropogenic or natural sources undergo various chemical and biochemical transformations in result of which they may accumulate in living organisms or bind bottom sediments. Determination of the total element concentrations in individual elements of the aquatic ecosystem does not provide information about the actual threat from xenobiotics. Contemporary approach to the environmental monitoring requires the use of the environment. Determining the environment pollution using bioindicators requires selection of appropriate animal and plant species, characterized by high abilities to accumulate a given xenobiotic. In case of water macrofauna it is also necessary to choose the organ in which an element accumulates in greatest quantities. The amount of elements accumulated in living organisms in first place depends on the forms in which they occur in the environment, which determines their bioavailability. In case of the elements which are microelements it is necessary to pay attention of their physiological role, the consequence of which is their increased accumulation in individual organs. The best method for an assessment of the threat posed to the environment by trace elements is determining bioaccumulation coefficient through an assessment of their accumulation in the organisms of subsequent trophic levels of the ecosystem [1]. Determining the environment pollution using bioindicators necessitates a selection of appropriate animal and plant species which are characterized by considerable abilities for a given xenobiotic accumulation. In case of water macrofauna it is also important to choose the organ in which an element accumulates in the biggest quantities [2, 3].

The paper aimed at determining iron accumulation in individual links of pond ecosystem food chain in conditions of intensive carp husbandry. On the basis of conducted research, the degree of pond pollution with this element was estimated and the element bioaccumulation coefficients were computed.

Material and methods

In 2008 research on iron cycling was conducted in a pond belonging to the Experimental Station of the Department of Ichtiobiology and Fisheries, University of Agriculture in Krakow, localized in Mydlniki, fed by the Rudawa river water. This is a commercial pond with an area of 4 ha. The investigations comprised determining iron content in water, bottom sediments, benthos and organs of carps (*Cyprinus carpio* L.).

Iron content in water was assessed thrice during the vegetation season. Samples were collected at the beginning of feeding season (in May), during the period of the most intensive fish feeding (in July) and in September by the end of fattening period. Water was taken from six points in the pond, whereas bottom sediments from the top layer of the pond bottom (0–5 cm) after the pond emptying. The pond was divided into eight zones and laboratory samples were collected from each one (two samples close to the outlet box, 4 samples from the central part of the pond and two in the vicinity of the outlet box). Bottom sediments were dried, sifted through a sieve with 1mm mesh and crumbled in a mortar. Samples of benthos organisms (*Diptera Chironomidae* larvae) were collected in the same spots. Iron concentrations in carp (*Cyprinus carpio* L.)

organisms were assessed in 25 randomly selected fish destined for consumption. The fish gender was determined (by organoleptic method), their age (insight into production documents) and mass of the analyzed carps (by gravimetric method). Fish originated from a three-year period of rearing, the weight fluctuated from 1500 to 2000 g. Carps were killed by decapitation and their organs (gills, muscles, livers and gonads) were prepared.

Obtained laboratory samples were subjected to wet mineralization in a closed system in a microwave mineralizer. The weighted portion for analyses was *ca* 0.5 g in conversion to dry mass. Biological material was dissolved in a mixture of HNO_3 and H_2O_2 (at 5:1 v/v ratio) of the acid, while bottom sediments in aqua regia (1:10). Water samples for analyses were condensed ten times. Iron concentrations in the obtained solutions were assessed by means of inductively coupled plasma atomic emission spectrometry (ICP-AES), on JY 238 ULTRACE apparatus (Jobin Yvon emission) at 238.04 nm wavelength. Iron limit of determination in the applied method was 0.0046 $mgFe \cdot dm^{-3}$. Uncertainty of measurement of applied methods was ±4 %. The limit of determination of the analyses was 0.155 $\mu g \cdot g^{-1}$ d.m. of biological material and 0.24 $\mu g \cdot g^{-1}$ d.m. of sediments. The correctness of iron analyses was verified using certified reference material CRM 16-050.

Result and discussion

Iron is an essential element for vertebrate animals. This element, being involved in oxygen transfer, respiratory chain reactions, DNA synthesis, and immune function. However, excess free iron promotes the formation of reactive oxygen species that are damaging to the host. The mechanisms of Fe uptake across the gills and intestine, is influence on geochemical prosperities of abiotic elements of ecosystem and life strategies of fish. Since there appears to be no regulated mechanism for iron excretion through the liver or kidney, to maintain iron balance both uptake by intestinal epithelial cells and recycling by macrophages are tightly controlled. Affect iron metabolism downloads on other elements. Ferric iron (Fe^{3+}) is first reduced to the ferrous (Fe^{2+}) form to the apical ferric reductase. Iron influenced of capable of transporting several other divalent metals, essential copper, zinc cobalt, nickel and manganese. A diet poor in iron can lead to excess accumulation of cadmium in organisms. If lead is not aware of such relationships [4]. Iron is an element, which is increasingly the subject of research related to aquatic ecosystems. Many research points to an important role of this element in the formation and development of the primary production of phytoplankton but only in seawater environments [5, 6]. Despite the propensity for iron oxidation in the freshwater environment it is not a limiting factor in lotic or lentic phytoplankton growth. The bioavailability of iron to organisms in freshwater is far greater than that of seawater.

Average iron content in surface waters fluctuates from 61 to 2680 $\mu gFe \cdot dm^{-3}$ Guarzu et al [7]. Its content in water is connected both with the intensity of its leaching from the parent rock and with industrial and municipal sewage discharge into the water bodies. An important source of iron in the environment are runoffs from roofs and hard surfaced areas. Mean content of iron in water of the analyzed pond was 988.2 μgFe · dm^{-3} (Table 1). No statistically significant differences were determined in water collected on various dates (Fig. 1). Water collected in August contained slightly smaller amounts of this element. Wisniowska-Kielian and Niemiec [8] assessed similar content of this metal in agricultural and recreational part of the Dunajec river catchment and only in the area of municipal and industrial sewage discharge iron concentrations were higher than obtained in the presented investigations. Fish [9] states that optimal iron content for the aquaculture animals remains within the range below 150 μgFe · dm^{-3}.

Table 1

Statistic parameters of the results

Statistic parameters	Water	Sedi-ments	Larvae	Organs of fish			
				Gills	Gonads	Muscle	Liver
	[μg · dm^{-3}]	[mg · kg^{-1} d.m.]					
Minimum	778.5	5088	1189	99.76	21.05	2.951	67.89
Maksimum	1305	9863	1997	395.9	354.5	70.76	207.8
Mean	988.2	8004	1583	192.8	95.70	37.62	114.1
Standard deviation	192.9	1602	319.7	70.13	76.82	20.00	35.63
Median	998.5	8533	1482	172.1	78.59	30.70	104.9
Deviation coefficient [%]	19.52	20.01	20.20	36.36	80.27	53.16	31.22

Oberholster et al [1] report that iron concentrations in the water of Loskop Lake in southern Africa range from 110 to 260 μgFe · dm^{-1}. At iron concentrations in water exceeding 800 μgFe · dm^{-1}, its compounds may start accumulating in bronchial epithelium in fish leading to possible changes of steroid hormone concentrations in blood plasma [10]. In aquatic environments where high iron concentrations, exceeding 1000 μg · dm^{-3} persist permanently, fish may develop defence mechanisms owing to which they are able to live and reproduce without toxicity symptoms [11], therefore the signals of negative effect of iron on aquaculture organisms are observed rarely. Iron bioavailability depends in the first place on its forms dissolved in water, which is

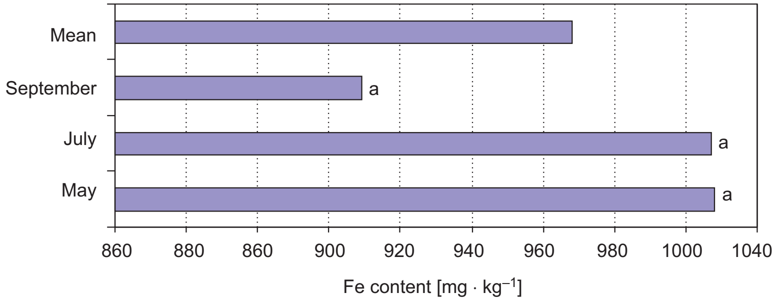

Fig. 1. Content of iron in water

associated not only with the total amount of this element but also with physicochemical, chemical and physical properties of water. Water pH and oxidation reduction conditions have the greatest effect on iron availability to fish. Increasing water pH causes precipitation of water insoluble iron carbonates which results in its immobilizing [12]. In fresh water processes of bivalent iron oxidation occur more intensively than in sea water, therefore its biodiversity in inland waters is much higher in comparison with seawaters. In high seas waters, deficiency of bioavailability iron often limits the amount of primary production [13]. Iron does not belong to toxic elements, but it affects the uptake of other elements which may cause their secondary deficiency [1]. It water it persists for a short time in an insoluble form. It precipitates to the sediments as hydroxides or insoluble trivalent iron salts. Ions of Fe^{3+} iron reveal a strong affinity to organic matter. In reservoirs with high content of seston organic fractions, faster processes of iron immobilization are observed in bottom sediments [14]. In the close to the bottom zone under conditions of oxygen deficiency, Fe^{3+} iron undergoes reduction forming water insoluble compounds. In this way it becomes available to benthos organisms. This element effect on the natural environment is observed among others as a change of physicochemical properties of bottom sediments, worsening the conditions of benthos organisms development. Liming the benthos and periphyton development leads to worsened biodiversity of the whole aquatic ecosystem and diminishes food resources for fish [15]. Iron plays an important role in processes of element cycling in aquatic ecosystem, particularly sulphur, phosphorus and heavy metals. Iron is of major importance for phosphorus sorption in aquatic environments. The element is important for binding heavy metals and sulphur released during organic matter mineralization, which may limit their toxicity [16].

In the sediments found to be very high iron content. The source of this element in aquatic sediments eroded from the debris basin and the precipitation of this element in the sediments as a result of self-purification processes. In the conditions of high oxidation-reduction potential is iron oxidation and their unsoluble compounds is precipitated as a salt be trivalent iron. Iron precipitates in the sediments in the form of carbonates, sulfides, phosphates. Mean content of iron in bottom sediments from the investigated pond ecosystem was 8004 mgFe · kg^{-1} (Table 1). Wisniowska-Kielian and Niemiec [8] noted higher iron concentrations in bottom sediments of the Dunajec river, reaching 7–25 g · kg^{-1}. Slight differences were registered in this element contents in samples collected from various parts of the pond. Iron in bottom sediments originates in the first place from processes of catchment erosion, whereas anthropogenic sources of this element are of minor importance. In research of Yuvanatemiya and Boyd [2], bottom sediments from unpolluted fish ponds contained only 150 mgFe · kg^{-1}. The authors registered much lower coefficient of sediment enrichment in relation to its content in water in comparison with the results obtained in the Authors' own studies. On the other hand, iron concentrations in the sediments from ponds which are receiving waters in Czech Republic, fluctuate from 100 to 1300 mg · kg^{-1} [17]. Iron content in the studied sediments was high and is characteristic for bottom sediments of basins whose catchments are developed from geological formations rich in this element or reservoirs intensively used antropogenically.

The most important representatives of benthic invertebrates in the studied ecosystem are the larvae of the chironomidae. These organisms are widespread in eutrophic reservoirs in the northern hemisphere, in mid-latitudes and can be found both in the environment of flowing and standing water. Because of its ecological functions associated with the decomposition of detritus and the most important item in the diet of benthos-eating fish, chironomidae larvae are a common subject of research in freshwater ecology interesting because they are the predominant part of benthic [18]. Chironomidae are a valuable group of organisms used in biological monitoring of environmental pollution [19]. Iron concentrations in benthos organisms of the investigated ecosystem fluctuated from 1189 to 1997 mgFe $\cdot$ kg^{-1} d.m., reaching average value on the level of 1583 mgFe $\cdot$ kg^{-1} d.m. (Table 1). Bioaccumulation coefficient of this element in *Diptera Chironomidae* larvae was respectively 1602 and 0.198 in relation to its level in water and bottom sediments (Table 2). Nurhasan et al [20] report iron concentrations in water insect larvae on rice fields in China on the level of 590 mgFe $\cdot$ kg^{-1} d.m. at much lower content of this element in the abiotic elements of the ecosystem. Contents approximate to obtained in the presented investigations the authors quoted above found in snails. Iron bioaccumulation coefficient in benthos organisms was over twice higher in the Authors' own research than presented by Nurhasan et al [20]. On the other hand, Foxall et al [21] stated iron content between 9170 and 12980 mgFe $\cdot$ kg^{-1} d.m. in endemic snail species from Tanganica Lake. High iron concentrations in water sediments and bottom fauna are specific for reservoirs in warm climate. Very high iron content in benthos organisms is the consequence of high accumulation of this element in sediments. Changes of oxidation-reduction conditions or changes of reaction in above-the-sediments water may lead to an immobilization of this metal or its accumulation in living organisms. Iron contents in benthos organisms of the analyzed ecosystem are high, which at high share of natural feed for carps may lead to a higher supply of this metal for fish.

Table 2

Bioaccumulation coefficients of iron in biotic part of environment

Parts of environment	Larvae	Gills	Gonads	Muscle	Liver
Water	1602	1951	96.84	38.07	115.5
Sedimets	0.198	0.024	0.012	0.005	0.014
Larvae	—	0.122	0.060	0.024	0.072

Iron is an element with strongly bioconcentration , especially in aquatic organisms that are at low levels of the trophic chain. The value of this coefficient in the fish can be even more than 1500. Very easy is captured through the skin, gills and epithelium. Accumulated mainly in the liver [22]. There is no documented studies in the literature demonstrating that this element is biomagnification. Iron deficiency is often observed that organisms inhabiting the ecosystems of the poor in this element, or in conditions of artificial breeding. Iron is routinely added to fish feeds in aquaculture. The concentrations of iron in the diet required to prevent signs of iron deficiency. for salmon required iron concentration in the feed is 60–100 mgFe · kg^{-1} for channel catfish 30 mgFe · kg^{-1}, and puffer fish 90–140 mgFe · kg^{-1}. A daily loss of iron by the freshwater fish is about 10–18 μg · kg^{-1} · day^{-1}. The uptake efficiency of iron from fish diet required to balance iron loss would have to be in the order of 0.7–1.2 %.

Bivalent form of iron Fe^{2+} is more available than $Fe^{3+,}$ but in oxic aquatic environments and at pH between 6.5–7.5 Fe^{2+} is oxidized to Fe^{3+}. In freshwater the oxidation rate of Fe^{2+} is considerably slower compare with than in seawater [23], and in these oxic environments iron is found as colloidal hydrous iron oxides that are not biologically available. The physio-chemical characteristics of seawater makes easier the formation of colloid aggregation. Fe^{3+} oxyhydroxide colloids, which may also be complexed with organic matter [24], settle out and the reducing environs of the anoxic zone or sediment results in Fe^{3+} reduction and Fe^{2+} leaches from the sediment generating an iron cycle. In the warm tine stratification of eutrophic reservoirs may result in an oxic zone extending only a few metres below the surface, and during the autumn or winter the breakdown of the thermocline as the lake cools results in the mixing of the bottom nutrient and iron rich waters. Based on these observations it would appear that there is a greater potential for iron uptake by the gills of freshwater fish compared to marine fish, but that the diet is probably the most important source of iron in both environments.

Carps are considered as organisms useful in the research on bioavailability of pollutants in the environment. They are organisms resistant to high concentrations of pollutants and reveal considerable abilities for these substances accumulation [23, 25].

Gills are important organ of ionic exchange in fish organism. Fish absorb and release metals from water through these organs. Iron is taken up by gills as free ions and chelates of this element. The other way of iron absorption by fish organism is alimentary canal. The ratio between iron absorption by gill and from alimentary canal determine the amounts of this metal in water and feed [26]. Iron uptake by fish gill epithelium is the most affected by water pH and its oxidation-reduction potential. In strongly alkaline and oxidative environment a limited iron uptake by fish gill epithelium is observed [27]. Precise regulation mechanism of iron quantity entering through gills and with feed has not been identified yet [28]. If iron occurs in aquatic environment in large quantities, its insoluble compounds (oxides or hydroxides and sulphites) may accumulate in gills, inhibiting gaseous and ionic exchange in fish [29]. In many aquatic environments, particularly saltwater bodies deficiencies of this element are observed [14]. In such environments fish often develop mechanisms of iron uptake from hardly available sources. Fish gill epithelium may produce substances which allow to absorb iron bound in insoluble compounds, *eg* as iron sulphites [30]. Iron content in gills of the analyzed fish was highly diversified and ranged from 99.76–395.9 mg · kg^{-1} d.m. with mean 192.8 mg · kg^{-1} d.m. (Table 1). Relative standard deviation was 36.6 %. No statistically significant differences of iron concentrations were observed in male and female gills (Fig. 2). High concentrations of this element in gills result from considerable blood supply in these organs. Uysal et al [31] report iron content in gills of various fish migrating from the area of Beymelek Lagoon in Turkey on a similar level

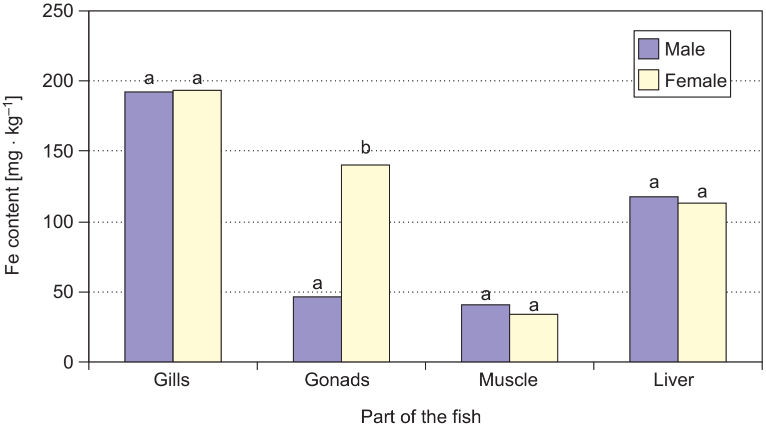

Fig. 2. Content of iron in following organs depending on sex

as the results obtained in the Authors' own investigations, however iron concentrations in fish muscles stated by these authors were several times lower. Under conditions of high iron concentrations in water, its increased concentrations in gills are observed connected with precipitation of this metal hydroxides in gill flakes. This element content in carp gills was over ten times lower than in benthos organisms. The metal bioaccumulation coefficient in relation to its concentrations in water and sediments was respectively: 195 and 0.024, while in relation to its content in benthos, the value of bioaccumulation coefficient was on the level of 0.122 (Table 2).

Iron content in carp muscles revealed high changeability fluctuating from 2.951 and 70.76 mgFe · kg^{-1} (Table 1). Mean content was 37.62 mgFe · kg^{-1} d.m. Relative standard deviation was 53.16 %. Muscles of male fish contained slightly more of this element. The differences were not statistically significant (Fig. 2). Nurhasan et al [20] assessed iron content in muscles of carps kept on rice fields and obtained results similar to presented in this paper despite much lower content of this element in abiotic environment components. Roos et al. [32], who report iron content in muscles of various fish species in fresh waters of Cambodia, point to a considerable diversification of this element content depending on fish species, ranging from 20 to over 360 mgFe · kg^{-1} d.m. The animal living environment has a lesser influence on iron concentrations [32]. Cooper at al [27] registered very high contents of iron, ranging from about 80 mg to over 150 mgFe · kg^{-1} d.m., in Danio rerio fish carcasses depending on this element quantity in feed. Foxall et al [21] report iron contents in muscles of 6 fish species from Tanganica Lake on the level from 29 to 38 mgFe · kg^{-1} d.m. Iron level in snails from this lake was much higher than noted in *Diptera Chironomidae* analysed in presented research. No effect of sampling localization was observed on iron accumulation level in fish tissues. Iron content in fish muscles is an important criterion of their usability for human consumption. Luczynska et al [33] report much lower amounts of this element in muscles of carps available in shops in Olsztyn.

Liver is the main place of iron accumulation in fish organism. This element concentration in this organ is a sensitive indicator of its availability in the environment but also health condition of fish [7, 34, 35]. The content of iron accumulated in livers of the analysed carps revealed the lowest changeability and fluctuated from 67.89 to 207.8 mgFe · kg^{-1} d.m. (Table 1) at an average content of 114.1 mgFe · kg^{-1} d.m. Male livers contained slightly bigger amounts of this metal, but the differences between males and females were not statistically significant. Coefficient of variation for all analyzed samples was 31 %. Iron bioaccumulation coefficient in the analysed fish livers was 115 in relation to its amount in water; 0.014 in relation to iron concentration in the sediments and 0.072 in relation to its content in benthos organisms.

Gonads are the organs where iron accumulation does not occur. Its concentrations in these organs is connected with their physiological functions. This element content in gonads showed a considerable changeability, fluctuating from 21.05 to 345.5 mgFe · kg^{-1} d.m. Mean content of this element was 95.7 mgFe · kg^{-1} d.m. (Table 1). A significant statistical differences were observed in this element content in testicles and ovaries. About thrice bigger amounts of iron were found in ovaries than in testicles.

Among all analysed organs, the highest amounts of iron were registered in gills, then in ovaries, in the liver and testicles, whereas the lowest content in muscles of the analysed carps. The ratio of iron content in these organs was 1 : 0.70 : 0.59 : 23 : 0.20. No statistically significant differences were registered between iron content in male and female organs, except its concentrations in gonads.

Conclusions

1. Water and bottom sediments from the ponds were characterized by high iron content.

2. Iron concentrations in individual fish organs was in the following order from the highest: gills > ovaries > liver > testicles > muscles.

3. Coefficient of iron enrichment was high in bottom sediments and characteristic for the ecosystems abundant in this element.

4. Iron content in benthos was very high, characteristic for the environments abundant in this element.

5. Iron bioaccumulation coefficient assumed much higher values in *Diptera* larvae organisms in comparison with the literature data, whereas in carp organisms its value was lower than presented in the subject literature.

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AKUMULACJA ŻELAZA W WYBRANYCH ELEMENTACH ŁAŃCUCHA POKARMOWEGO EKOSYSTEMU STAWOWEGO

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Abstrakt: Celem pracy było określenie akumulacji żelaza w poszczególnych ogniwach łańcucha pokarmowego ekosystemu wodnego w warunkach ekstensywnego chowu karpi. Na podstawie zawartości tego pierwiastka w biotycznych i abiotycznych elementach ekosystemu oszacowano stopień jego zanieczyszczenia. Badania wykonano w stawie hodowlanym, położonym w Mydlnikach, zasilanym wodą z rzeki Rudawa. Z badanego stawu pobrano: wodę, osad z dna stawu, organizmy bentosu reprezentowane przez larwy muchówek z rodziny ochotkowatych, a także karpie, z których wypreparowano narządy w największym stopniu związane z metabolizmem metali (skrzela, gonady, wątroba i mięśnie). We wszystkich próbkach oznaczono zawartość żelaza metodą emisyjnej spektrometrii atomowej w aparacie JY 238 ULTRACE Jobin Yvon Emission. Mineralizację próbek wykonano metodą na mokro w systemie zamkniętym z wykorzystaniem energii mikrofalowej. Na podstawie uzyskanych wyników stwierdzono, że w badanym ekosystemie nie ma zagrożenia zatrucia żelazem. Zawartości tego pierwiastka w wodzie i osadach dennych są porównywalne do innych akwenów, pochodzenia antropogennego i naturalnego zasobnych w ten pierwiastek. Stwierdzono dużą wartość współczynnika wzbogacenia osadów w żelazo w stosunku do jej zawartości w wodzie. Zawartość żelaza w organizmach bentosu przyjmowała duże wartości, od 1189 do 1997 mg · kg^{-1} s.m. Wartości współczynnika bioakumulacji żelaza w larwach ochotkowatych w stosunku do jego ilości w wodzie i osadach wynosiły odpowiednio 1602 i 0,198. W organizmach badanych ryb zawartość żelaza kształtowała się w zakresie 2,951 do 395,9 mg · kg^{-1} s.m. Najwięcej tego pierwiastka stwierdzono w skrzelach, następnie w wątrobie, gonadach, a najmniej żelaza akumulowały mięśnie. Dane literaturowe wskazują, że zawartość żelaza w rybach zależy od ilości tego pierwiastka w środowisku, ale w większym stopniu od właściwości abiotycznych elementów środowiska. Sumaryczna zawartość żelaza w osadach dennych i wodzie nie pozwala ocenić zagrożenia środowiska zanieczyszczeniem żelazem, dlatego tak ważne jest stosowanie bioindykacji. Zawartość żelaza w skrzelach i wątrobie ryb jest najbardziej miarodajnym wskaźnikiem zanieczyszczenia środowiska związkami żelaza. Wartość współczynnika bioakumulacji żelaza w skrzelach badanych karpi wynosiła w stosunku do jej zawartości w wodzie i osadach dennych odpowiednio 195,1 i 0,024 natomiast w stosunku do jego zawartości w larwach owadów wartość tego parametru wynosiła 0,122. Dane literaturowe wskazują, że poziom akumulacji żelaza w organizmach żywych jest uzależniony od środowiska w którym żyją.

Słowa kluczowe: żelazo, bioakumulacja, łańcuch pokarmowy, akwakultura, karp

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TEMPERATURE AND OXYGEN PROFILES OF RESTORED WATER BODIES

STRUKTURA TERMICZNO-TLENOWA WÓD ZRENATURYZOWANYCH ZBIORNIKÓW WODNYCH

Abstract: The study covered three lakes: Nowe Wloki (with two pools – Main Basin and Northern Bay), Setalskie Duze and Setalskie Male – connected by the Setal Stream (Struga Setal) to form a riverine-lacustrine system. Due to their specific location (slope), the investigated water bodies form a cascade system. They are situated 25 km from the city of Olsztyn, in the Dywity municipality (Olsztyn Lakeland), in an agricultural catchment. Due to their low average depth (1 to 2 m), the analyzed water bodies can be classified as polymictic.

The aim of this study was to analyze the temperature and oxygen profiles of water bodies restored approximately 30 years ago. The profiles were determined during winter stagnation (2005 and 2006) and summer stagnation (2007).

An analysis of temperature and oxygen conditions performed in the summer confirmed close correlations between the studied parameters. All lakes were characterized by incomplete thermal and oxygen stratification, typical of shallow water bodies. The oxygen profiles determined in the winter showed a temperature distribution pattern characteristic of reverse thermal stratification. In all investigated water bodies, surface water temperature was close to 0 ^{o}C, and it increased gradually from a depth of 30–50 cm. During winter stagnation, the highest dissolved oxygen content was noted in the top layer of water under the ice, and oxygen concentrations varied widely between years. The lowest oxygen content was observed at the bottom, and critically low values (from 0.16 $mgO_2 \cdot dm^{-3}$ to 0.29 $mgO_2 \cdot dm^{-3}$), were recorded during the severe winter of 2006, when ice cover thickness reached 40 cm and organic matter decomposition and aerobic respiration processes led to almost complete oxygen depletion.

Keywords: restored water bodies, thermal-oxygen profiles, oxygen saturation

Introduction

Temperature and oxygen are among the most important abiotic characteristics of natural aquatic ecosystems. Oxygen plays a key role in all chemical and biochemical

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processes in water bodies, and it is essential for the survival of aquatic organisms. Oxygen is needed for aerobic respiration processes which reduce the concentrations of various pollutants in water. Oxygen deficiency supports anaerobic processes which lead to a deterioration in water quality and limit biological processes.

In shallow (polymictic) water bodies, waters mix multiple times during the year, making the water body more susceptible to environmental stress. Water mixing also significantly influences temperature and oxygen distribution in the vertical profile. In water bodies, the main sources of oxygen are the atmosphere and photosynthesis processes.

The transfer of oxygen across calm water surfaces is relatively ineffective, and oxygen is able to penetrate deeper layers of the water body only in the process of water mixing. Oxygen conditions in water bodies are determined not only by mixing dynamics, but also by the level of pollution.

Substances that are leached from farmland have a highly adverse impact on the quality of surface waters. The inflow of fertilizers into aquatic environments supports massive growth of algae. High density of the algae leads to higher oxygen consumption due to the decomposition of algal biomass in deeper strata of the water body. Oxygen depletion supports decomposition processes, and the loss of oxygen in deeper water layers initiates the release of minerals from bottom deposits where nutrients are immobilized in the process of organic matter sedimentation [1].

Excessive accumulation of organic matter in water bodies contributes to eutrophication, and it makes lakes very short-lived sites on the geological time scale that is measured in terms of millennia. An increase in fertility levels in catchments, in particular in rural areas, can be observed even over a period of several years [2, 3].

Objective and description of the analyzed sites

The solubility of oxygen in water is largely determined by temperature, and the concentrations of dissolved oxygen decrease with a rise in temperature. For this reason, oxygen levels fluctuate significantly throughout the year.

The aim of this study was to analyze the temperature and oxygen profiles of water bodies restored approximately 30 years ago, located in rural areas. The profiles were determined during winter stagnation (2005 and 2006) and summer stagnation (2007). Owing to the considerable surface area of lakes Nowe Wloki and Setalskie Duze, temperature and oxygen profiles were analyzed in eastern as well as western sections of those water bodies. The profiles of Lake Setalskie Male were studied in the deepest section. The only exception was made during the harsh winter of 2006, when the investigations in Lake Setalskie Duze were restricted to deep waters. Measurements were performed with the use of an oxygen sensor with automatic temperature compensation (WTW OXI Top OC 100). Water pH, electrolytic conductivity and redox potential were determined. In summer, water transparency was additionally measured with the Secchi disc.

The study covered three lakes: Nowe Wloki (with two pools – Main Basin and Northern Bay, connected by a stream), Setalskie Duze and Setalskie Male. The studied

Table 1

Morphometric parameters of the studied water bodies and catchment area characteristics (total catchment and subcatchments)

Site	Surface area [ha]	Average depth [m]	Catchment	Area [ha]	Slope [%]	Type of land use
Lake Nowe Wloki	19.7	1.5	*Total catchment*	**408.19**		52 % – arable land, 13 % – water, 5 % – forests, 29 % – meadows, 1 % – developed area
			Direct catchment	145.73	3.1	
Main basin	15.5	1.5	• catchment area of the Setal stream feeding into the main basin	77.62	2.9	60 % – arable land, 10 % – forests, 29 % – meadows, 1 % – developed area
			• catchment area of the canal feeding into the main basin	11.96	6.6	94 % – arable land, 1 % – water, 6 % – meadows
Northern bay	4.3	1.5	• catchment area of the drainage ditch feeding into the northern bay (covered by the catchment area of the northern bay in its entirety)	172.88	1.7	66 % – arable land, 7 % – forests, 21 % – meadows, 6 % – developed area
Lake Setalskie Duze	41.4	2.5	*Total catchment*	**757.23**		54 % – arable land, 19 % – water, 10 % – forests, 16 % – meadows, 2 % – developed area
			Direct catchment	199.29	1.7	
			• indirect catchments (including the catchment area of Lake Nowe Wloki)	408.19		
			• catchment area of the stream feeding into the lake	149.75	4.4	86 % – arable land, 1 % – water, 3 % – forests, 10 % – meadows
Lake Setalskie Male	8.0	1.1	*Total catchment*	**883.82**	3.8	82 % – arable land, 10 % – water, 1 % – forests, 6 % – meadows, 1 % – developed area
			Direct catchment	126.59		
			• indirect catchment, including the catchment areas of lakes Nowe Wloki and Setalskie Duze	757.23		

objects were drained in the 19th century during a comprehensive land improvement project to create agricultural grassland. Field flooding was a recurring problem in the region due to excessive water logging. In view of the need for small retention reservoirs and fire water reservoirs in rural areas, the discussed water bodies were restored at the turn of the 1970s and the 1980s as part of a land reclamation scheme initiated by the Regional Farmland Improvement Authority in Olsztyn. The lakes were created as a result of water damming on the Setal Stream. Due to their specific location (slope, 3.1–6.6 %), the investigated water bodies form a cascade system (Table 1). They are located in the Protected Landscape Area in the Valley of Middle River Lyna, 25 km from the city of Olsztyn, in the north-eastern part of Dywity municipality (Fig. 1). The studied riverine-lacustrine system is situated in a rural, scantily wooded area, used for agricultural purposes (Table 1).

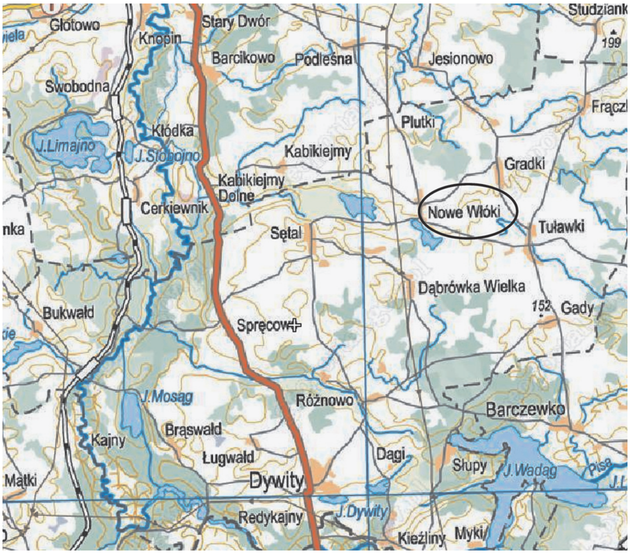


Fig. 1. General map of the investigated area. Source: geoportal.gov.pl

Lake Nowe Wloki (19.7 ha) – the southern part of the lake, which is the main basin, has an elongated profile, and it is adjacent to farmland on the right bank and meadows on the left bank. The northern bay has a much smaller area, and it is found in the vicinity of a road leading to Setal. In the north, the lake directly neighbors three farming estates without livestock. The upper section of Setal Stream feeds into the main basin of the lake. On the eastern side of the lake, there is a canal that drains the catchment occupied by farmland in more than 94 %. In the catchment on the northern side of the lake there is the village of Nowe Wloki which does not operate a sewer system. The area is drained by a drainage ditch which feeds into the northern bay of Lake Nowe Wloki. Lake Nowe Wloki is situated at the highest altitude (142.5 m above sea level), and it connects with Lake Setalskie Duze (124 m above sea level) via the Setal Stream. Lake Setalskie Duze is the largest of the studied objects, with an area of 41.4 ha. Its eastern part features a bay, and the western, much larger part is situated in the catchment occupied by farmland in more than 54 %. The lake's total catchment area incorporates the inflows from the catchment of the higher situated Lake of Nowe Wloki. The western part of the catchment features three land plots with holiday cottages made of brick. Water is evacuated from Lake Setalskie Duze via a ditch, and it is carried along farm fields to Lake Setalskie Male (8 ha), separated from Lake Setalskie Duze by a (straight line) distance of approximately 300 m. Lake Setalskie Male is situated in a catchment which, together with the catchments of Lake Nowe Wloki and Lake Setalskie Duze, has a total surface area of 883.82 ha.

Due to their low average depth (≤ 2.0 m), the analyzed water bodies can be classified as polymictic (Table 1, Fig. 2).

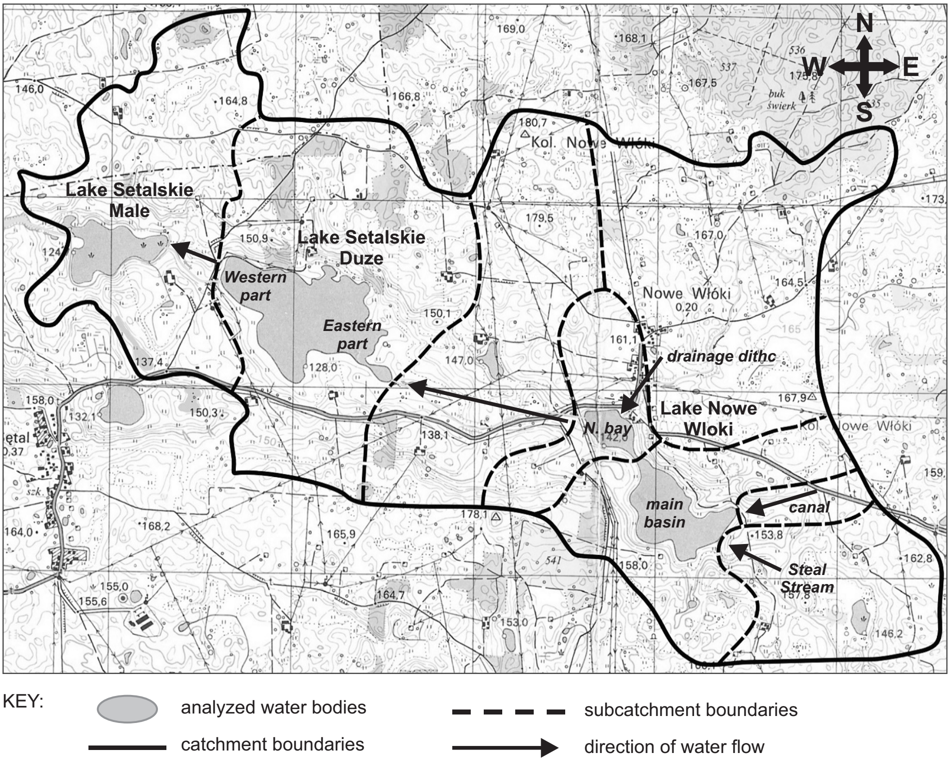
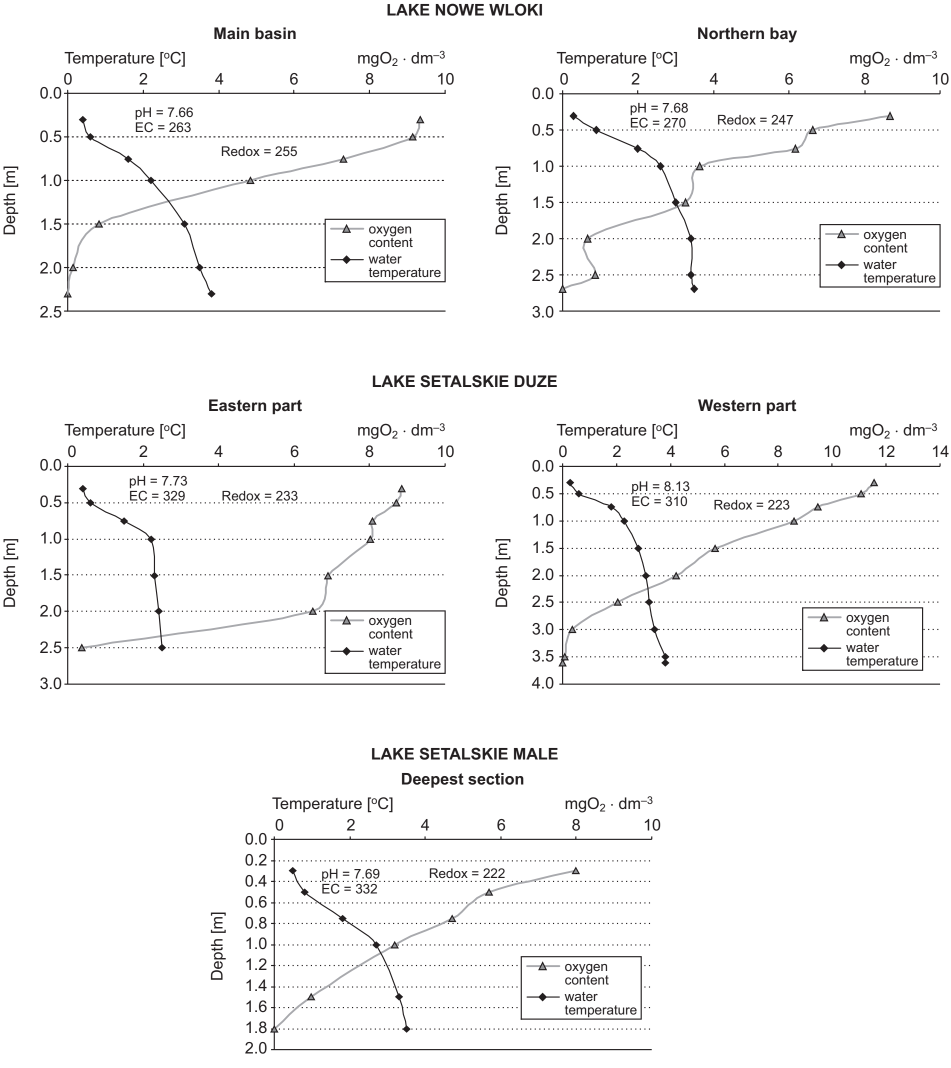


Fig. 2. Location of the analyzed sites

Results and discussion

The oxygen profiles determined in winter showed a temperature distribution pattern characteristic of reverse thermal stratification. Due to the presence of ice cover, temperature profiles in all studied lakes differed in comparison with the summer season. Low water oxygenation is connected with ice formations which make it difficult for atmospheric oxygen to dissolve in water, which is also confirmed by the research others authors [4]. In all investigated water bodies, surface water temperature was close to 0 °C, and it increased gradually from a depth of 30–50 cm, to reach around 3–4 °C at the bottom. In the profiles determined in the winter of 2005, a clear temperature gradient was observed at a depth of 0.5 to 1.5 m (1.7 to 2.8 °C), whereas a smoother temperature distribution pattern was reported in the vertical profile in the winter of 2006 when the thickness of ice cover on the studied lakes reached 40 cm (Figs. 3 and 4). Water cooling is directly dependent on the lake's depth and water volume. Shallow bodies of water are characterized by low thermal inertia [5].


LAKE NOWE WLOKI

Main basin

Northern bay

LAKE SETALSKIE DUZE

Eastern part

Western part

LAKE SETALSKIE MALE

Deepest section

Fig. 3. Temperature and oxygen profiles in the analyzed flow-through lakes in the winter of 2005

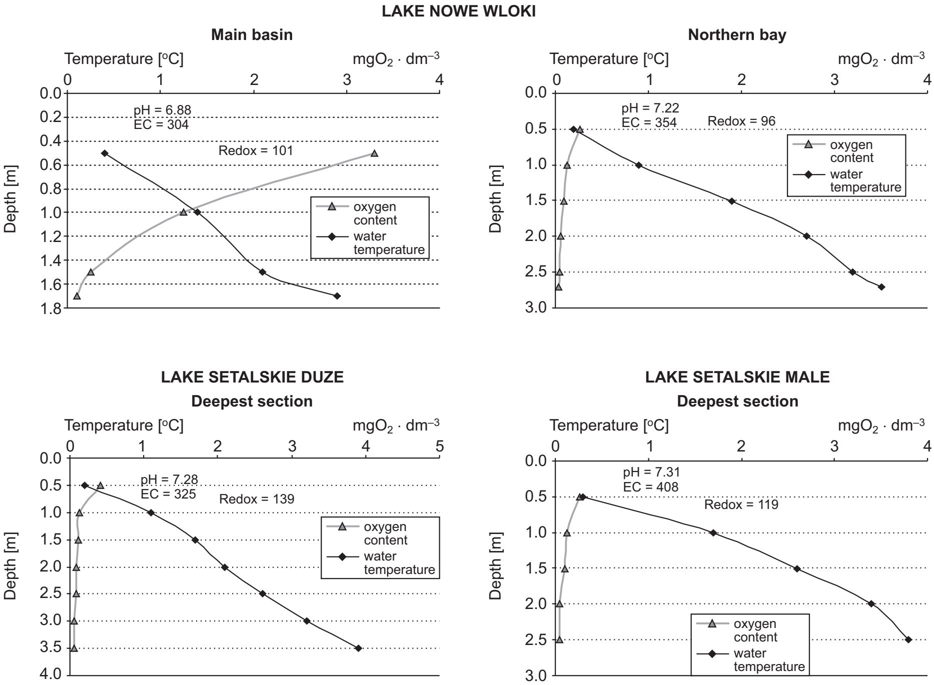
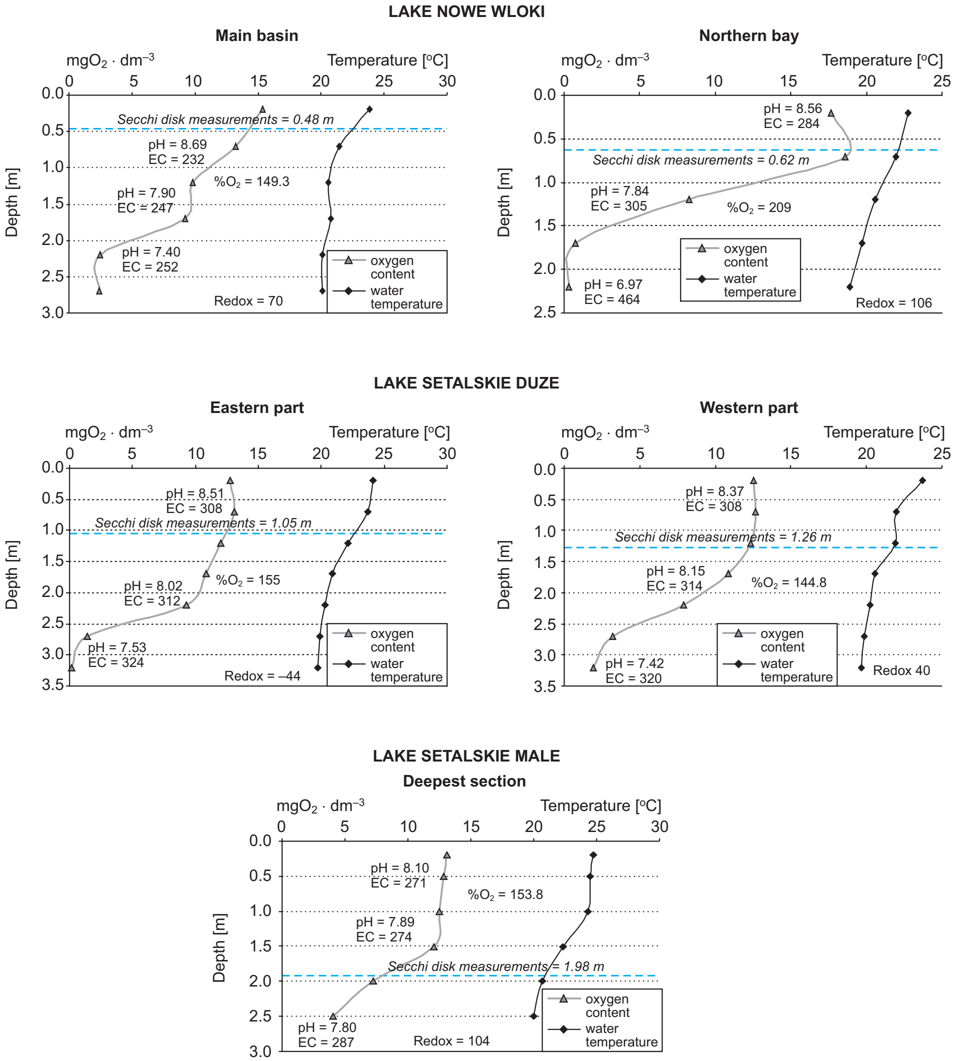


Fig. 4. Temperature and oxygen profiles in the analyzed flow-through lakes in the winter of 2006. * In 2006, the measurements in Lake Setalskie Duze were performed in the deepest section

During winter stagnation, the highest dissolved oxygen content was noted in the top layer of water under the ice, and oxygen concentrations varied widely between years. The winter of 2005 was milder (temperature in January –0.6 °C), and oxygen content near the surface layer of water ranged from 7.98 $mgO_2 \cdot dm^{-3}$ in Lake Setalskie Male to 11.55 $mgO_2 \cdot dm^{-3}$ in the western part of Lake Setalskie Duze (Fig. 3). In the winter of 2006 (temperature in January –8.3 °C), oxygen content was significantly lower in the range of 0.26 $mgO_2 \cdot dm^{-3}$ in the northern bay of Lake Nowe Wloki to 0.42 mg $O_2 \cdot dm^{-3}$ in the western part of Lake Setalskie Duze (Fig. 4). Oxygen concentrations in the main basin of Lake Nowe Wloki were determined at 3.3 $mgO_2 \cdot dm^{-3}$, indicating that the lake's oxygen resources had not been completely depleted despite the presence of ice cover. The above could be attributed to the fact that low temperatures slow down the oxidation of organic matter in bottom deposits, thus preventing complete oxygen depletion at the deepest strata of the water body. In the main basin of the lake, light penetrating the ice cover was used by the remaining phytoplankton in the photosynthesis process, thus increasing oxygen supply. Oxygen concentrations in the northern bay of the lake were significantly lower (0.27 $mgO_2 \cdot dm^{-3}$) due to higher levels of biogenic pollutants which are regularly supplied to the lake by the drainage ditch from a nearby village with no sewer system. The noted drop in oxygen levels was significant, and it led to fish oxygen starvation and death. During the severe winter of 2006, when ice cover thickness reached 30–40 cm, organic matter decomposition and aerobic respiration processes led to almost complete oxygen depletion in the studied water bodies (except for the main basin of Lake Nowe Wloki).

An analysis of temperature and oxygen conditions performed in the summer confirmed close correlations between the studied parameters. All lakes were characterized by incomplete thermal and oxygen stratification, typical of shallow water bodies. In summer, intense water heating led to a rapid increase in water temperature over a short period of time. The temperature of top water layers in the studied lakes ranged from 22.7 ^{o}C to 24.7 ^{o}C, and it decreased to around 18–20 ^{o}C at the bottom. The highest water temperature was noted in Lake Setalskie Male (Fig. 5).



LAKE NOWE WLOKI

Main basin

Northern bay

LAKE SETALSKIE DUZE

Eastern part

Western part

LAKE SETALSKIE MALE

Deepest section

Fig. 5. Temperature and oxygen profiles in the analyzed flow-through lakes in the summer of 2007

Shallow lakes have a thermal regime that is characteristic of polymictic water bodies. Permanent water circulation contributes to a uniform temperature profile and free oxygen distribution [6]. In the studied lakes, oxygen distribution patterns were correlated with temperature curves. The vertical profile of dissolved oxygen is illustrated by oxygen curves characteristic of eutrophic lakes which have a limited trophogenic zone and contain large quantities of organic matter that cannot be effectively mineralized in the oxygen-rich epillimnion. The oxygen curve has a clinograde profile which points to a decrease in assimilation processes and a rapid drop in dissolved oxygen levels to the point of complete depletion.

In all studied lakes, maximum values were noted in the layer between the lake's surface and a depth of 1.7 m (excluding the northern bay of Lake Nowe Wloki). At the above depth, dissolved oxygen concentrations were reported in the range of 9.21 $mgO_2 \cdot dm^{-3}$ in the main basin of Lake Nowe Wloki to 12.87 $mgO_2 \cdot dm^{-3}$ in Lake Setalskie Male. In the northern bay of Lake Nowe Wloki, oxygen concentrations were most similar (8.3 $mgO_2 \cdot dm^{-3}$) in the shallower zone at a depth of 1.2 m. Extensive growth of vegetation characteristic of wetland ecosystems, including sedge, common reed and bulrush, led to intensified oxygen consumption to support plant respiration, lowering oxygen concentrations in water. In the vertical profile of the northern bay, a significant drop in oxygen levels was observed at a depth of 1.2 m, and the difference in oxygen concentrations between a depth of 1.2 m and 1.7 m reached 7.57 $mgO_2 \cdot dm^3$ (Fig. 5).

Oxygen saturation in the studied lakes was very high in the range of 145 % to 155 %, and the highest saturation levels of 209 % were noted in the northern bay of Lake Nowe Wloki. High oxygen saturation is characteristic of eutrophic water bodies with a high level of primary production [7, 8]. In summer, high levels of dissolved oxygen result from photosynthesis and the release of free oxygen due to strong light penetration and the growth of aquatic vegetation [9]. In the summer season, oxygen saturation exceeds 100 %, as demonstrated in the studied lakes (Fig. 5).

In the analyzed lakes, a clear drop in the vertical profile of dissolved oxygen was determined at a depth of 1.7 m (excluding the northern bay of Lake Nowe Wloki – at a depth 1.2 m), and the lowest concentrations (from 0.16 to 4.07 $mgO_2 \cdot dm^{-3}$) were noted in the bottom layer. The lowest oxygen concentrations were reported in the eastern part of Lake Setalskie Duze (0.16 $mgO_2 \cdot dm^{-3}$) and the northern bay of Lake Nowe Wloki (0.29 $mgO_2 \cdot dm^{-3}$), *ie* the shallower parts of the studied lakes (Fig. 5). The above resulted from intensified mineralization of organic matter which was produced in the lake and stored in bottom deposits [7, 10].

In periods of stagnation, the differences in oxygen concentrations at various depths result from the release of oxygen during photosynthesis in surface layers as well as the uptake of oxygen for plant respiration and oxidation reactions, which are most intense in layers with a high content of organic matter [10].

Negative redox potentials were determined in the eastern section of Lake Setalskie Duze and the northern bay of Lake Nowe Wloki at – 106 mV and – 44 mV, respectively. The above is indicative of intensified reduction reactions which, if they persist for longer periods of time, are generally accompanied by the release of H_2S and NH_4 (due to decomposition) (Fig. 5).

In view of the above, it can be assumed that the vertical profile of oxygen distribution in various seasons of the year is a reflection on turbulent water mixing processes, the intensity of organic processes and hydrochemical reactions. Dissolved oxygen saturation is a function of the lake's productivity and the degree of environmental pollution in the aquatic ecosystem [7, 8].

The pH and electrolytic conductivity (EC) of lake water decreased with depth. High EC values in bottom layers also point to an increase in the mineral content of bottom sediments. Maximum EC values ($464\ \mu S \cdot cm^{-1}$) were also reported in the northern bay of Lake Nowe Wloki, which is situated in the direct vicinity of farm buildings, and in the eastern part of Lake Setalskie Duze ($324\ \mu S \cdot cm^{-1}$) where cattle are grazed on grasslands neighboring this part of the catchment area (Fig. 5).

Secchi disk measurements revealed the highest water transparency in Lake Setalskie Male (1.98 m) where color and turbidity values were low. The lowest transparency values were determined in Lake Nowe Wloki at 0.40 m in the main basin and 0.62 m in the northern bay. In the discussed lake, water had a greenish color which is characteristic of algal blooms (Fig. 5).

Conclusions

The results of our study confirmed the unsatisfactory condition of water bodies that had been restored more than 30 years ago. The ecological status of the studied lakes is similar to that of small water bodies in the nearby Olsztyn Lakeland. Oxygen conditions in the examined lakes varied significantly, and the northern bay of Lake Nowe Wloki showed the highest levels of oxygen depletion due to local conditions (proximity of farmland and rural settlement without a sewer system). The dissolved oxygen content of the analyzed water bodies indicate that with the current pattern of ecological succession, the lakes may soon reach the hypertrophic stage.

In additional to natural factors, the adverse effects of anthropogenic pressure have a particularly strong influence on the rate of changes in the relatively recently restored lakes in rural areas.

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STRUKTURA TERMICZNO-TLENOWA WÓD ZRENATURYZOWANYCH ZBIORNIKÓW WODNYCH

Katedra Melioracji i Kształtowania Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Badaniami objęto trzy zbiorniki wodne: jezioro Nowe Włóki (o dwóch plosach – basen główny i zatoka północna), jezioro Sętalskie Duże i jezioro Sętalskie Małe, połączone Strugą Sętal w jeden system rzeczno-jeziorny. Obiekty te ze względu na charakterystyczne położenie (spadki terenu) tworzą układ kaskadowy. Położone są one 25 km od Olsztyna w gminie Dywity (Pojezierze Olsztyńskie) w zlewni o wyraźnym ukierunkowaniu rolniczym. Analizowane akweny ze względu na małą głębokość średnią (od 1 do 2 m) należą do polimiktycznych.

Celem pracy była analiza termiczno-tlenowa wód zbiorników wodnych, odtworzonych przed około 30 laty. Profile zostały wykonane zarówno w okresach stagnacji zimowej (2005 i 2006 r.), jak i letniej (2007 r.).

Badania stosunków termiczno-tlenowych wykonanych latem wykazały dużą zbieżność elementów temperatury i tlenu. We wszystkich jeziorach stwierdzona została charakterystyczna dla wód płytkich niepełna stratyfikacja termiczno-tlenowa.

Wykonane zimowe profile tlenowe wykazały charakterystyczny układ dla temperatur, kiedy to zachodzi zjawisko stratyfikacji odwróconej – katotermii. We wszystkich badanych zbiornikach temperatura wody przy powierzchni była zbliżona do 0 ^{o}C i od głębokości około 30–50 cm stopniowo rosła. Największa zawartość tlenu rozpuszczonego w czasie stagnacji zimowej znajdowała się w górnej warstwie, tuż pod lodem i wyraźnie różniła się w poszczególnych latach. Najniższe stężenia O_2 występowały przy dnie, z krytycznie niskimi wartościami (od 0,16 $mgO_2 \cdot dm^{-3}$ do 0,29 $mgO_2 \cdot dm^{-3}$) odnotowanymi w akwenach w czasie bardzo ostrej zimy 2006 r., kiedy to pokrywa lodowa sięgała 40 cm. Wówczas procesy rozkładu materii oraz procesy oddychania tlenowego organizmów doprowadziły prawie do całkowitego zużycia tlenu w zbiornikach.

Słowa kluczowe: profile termiczno-tlenowe, odtworzone zbiorniki, nasycenie tlenem

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Mirosław SKORBIŁOWICZ[1]

PHOSPHORUS IN BOTTOM SEDIMENTS OF RIVERS FROM WITHIN THE UPPER NAREW CATCHMENT

FOSFOR W OSADACH DENNYCH RZEK Z OBSZARU ZLEWNI GÓRNEJ NARWI

Abstract: The aim of present study was to determine the content of phosphorus in bottom sediments from rivers of the Upper Narew catchment area. The study deals with tracing the changes of phosphorus in bottom sediments on the background of the spatial distribution of point sources of this nutrient, and identifying the main factors of its enrichment related to morphometry and management of catchment. The study was focused on the Narew River in 10 measurement sections within the stretch Bondary – Tykocin and the Supraśl River, on which six measurement points were selected. During the selection of the bottom sediment sampling sites, the presence of sites where the aquatic environment is improved in phosphorus (mainly sewage treatment plants), was adopted as the main criterion. Samples for analyses were also collected from 17 smaller and larger tributaries of Narew River. The highest contents of phosphorus in bottom sediments were found in Narew River (1.31 gP · kg^{-1} d.m.), while the lowest in river Strabelka (0.10 gP · kg^{-1} d.m.). Comparison with other research revealed that studied sediments were characterized by a typical content of phosphorus, and locally increased amounts of this element are the result of limited, however still existing anthropogenic pressure. The results indicate a relationship between phosphorus in bottom sediments and the nature of particular rivers catchments, including the amount of sewage discharged into these rivers.

Keywords: phosphorus, bottom sediments, rivers, sewage

Introduction

Phosphorus in bottom sediments is a subject of research for its role in the eutrophication of surface waters. The sediments can raise the load of phosphorus to the super-sediment water at a level comparable to an external source [1].

Studies of phosphorus in bottom sediments are a key factor for understanding the cycle of the element in rivers and lakes. This is also essential in the management and reclamation projects related to water reservoirs and rivers [2].

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It should be emphasized the importance of this research in the context of pollution of the Baltic Sea by phosphorus compounds. The total load of the Baltic Sea by the phosphorus from Polish sources constituting 37 % of the overall pollution is transported from the waters of the rivers [3]. These inputs include inputs from natural background sources as well as anthropogenic sources.

Bottom sediments are an important link in the river bed. They have a buffering property; they may bind certain minerals and elements from waters and transfer them to waters. The chemical composition of bottom sediments, including the amount of phosphorus, is affected by natural and anthropogenic factors such as geological and geomorphological structure, climatic conditions (critical for rock weathering, mobilization, migration, and accumulation of elements within the environment), as well as the degree of urbanization and industrialization of a given area [4].

Phosphorus inputs to rivers are traditionally classified as either point or diffuse, although there is some overlap between these classifications [5].

The aim of present study was to determine the content of phosphorus in bottom sediments from rivers of the Upper Narew catchment area. The study deals with tracing the changes of phosphorus in bottom sediments on the background of the spatial distribution of point sources of this nutrient, and identifying the main factors of its enrichment related to morphometry and management of catchment.

Material and methods

The study was focused on the Narew River in 10 measurement sections within the stretch Bondary – Tykocin (Fig. 1) and the Supraśl River, on which six measurement points were selected.

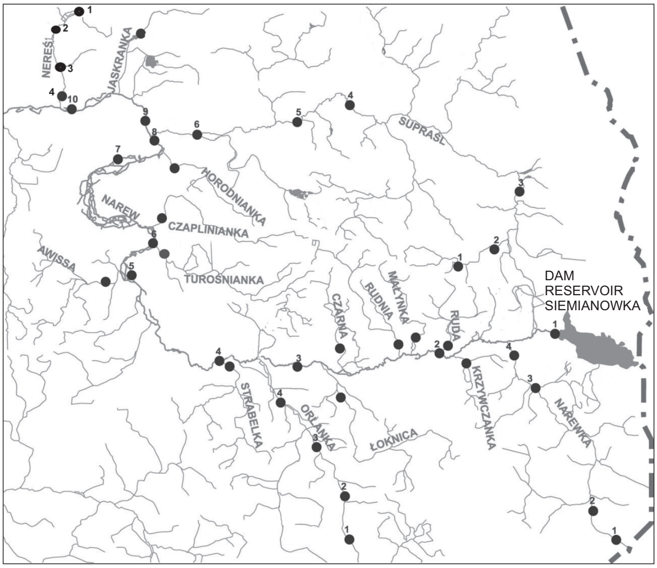

Fig. 1. Localization of bottom sediments sampling points within upper Narew River catchment

During the selection of the bottom sediment sampling sites, the presence of sites (mainly sewage treatment plants), where the aquatic environment is enriched in phosphorus, was adopted as the main criterion. Samples for analyses were also collected from 17 smaller and larger tributaries of Narew River (Fig. 1). Table 1 presents characteristics of studied rivers and their catchments.

Table 1

Characteristics of studied rivers and their catchments [8]

River	Structure of catchment area				Length of rivers	Catchment area	Amount of domestic sewage discharged to rivers
	Urbanized areas	Arable lands	Meadows and pastures	Forests			
	[%]				[km]	[km^2]	[m^3 · d^{-1}]
Narew	6	40	20	25	199	6270	444
Suprasl	3	39	28	30	94	1800	650
Narewka	3	15	12	70	48	680	385
Orlanka	6	37	53	4	53	521	70
Neresl	10	59	21	10	39	291	3120
Jaskranka	8	33	41	15	22	120	263
Czarna	4	47	29	20	16	45	—
Ruda	4	43	23	30	12	60	—
Rudnia	4	47	20	22	23	90	—
Czaplinianka	5	43	28	18	17	80	—
Łoknica	3	59	23	15	28	183	—
Awissa	8	54	19	14	15	130	3738
Mienka	3	60	26	11	7	60	—
Turosnianka	5	53	30	12	22	144	—
Horodnianka	15	40	26	18	18	76	900
Krzywczanka	4	52	24	20	10	25	—
Malynka	3	63	14	20	15	60	—
Strabelka	3	45	30	21	16	33	—

Number of selected measurement points on these rivers depended on the catchment area and the river length, and was usually reduced to two, three or four (springs, points in the middle section of the river, estuary). The study was conducted once in 2007. Several individual (7–10) samples of the surface layers of bottom sediments (0–10 cm) in the coastal zone were collected from every selected control-measurement point. The coastal zone is characterized by the deposition of suspended material [6]. After mixing, the test material composed a representative sample.

Samples were transferred to the cuvettes and allowed to completely dry. Air-dry material was ground in an agate mill, dried at a temperature of 105 ^{o}C to constant weight and particular aliquots of samples were prepared for determination. The particulate samples were sieved through a sieve with a mesh of 0.2 mm. This is the type of deposit fractionation commonly used in the geochemical mapping works [7].

Fractions of less than 0.2 mm grain size were used for further study. Sediment samples mineralized in a mixture of sulfuric acid and hydrogen peroxide in acid reflux. After mineralization in the solutions phosphorus were examined by colorimetric method with ammonium molybdate and ascorbic acid.

A total of 41 results of phosphorus content were achieved (Table 2). Arithmetic mean values and standard deviation (SD) of the results referring to sediments from rivers Narew, Supraśl, Narewka, Orlanka and Neresl were calculated. The relationships between results were determined by calculating the Spearman correlation coefficient "*r*" (nonparametric test).

Results and discussion

Phosphorus contents in studied bottom sediments ranged from 0.10 g · kg^{-1} to 3.90 g · kg^{-1} d.m. (Table 2), while arithmetic mean of these contents was 0.57 g · kg^{-1} d.m. [9].

The concentrations of total phosphorus in sediment of Xiangxi River in China ranged from 0.76 to 1.44 g · kg^{-1}. The Xiangxi River is 469.7 km long, with a watershed area of 3,099.4 km^2 [9].

Results showed that the content of total P in the sediments in Daliao River, China, ranged from 0.23 to 0.84 g · kg^{-1}, with an average of 0.55 g · kg^{-1}. The Daliao River system consists of the Daliao River, Hun River and Taizi River, with 94, 415 and 413 km in length, draining 1390, 11,500 and 13,900 km^2 of land area, respectively [10].

The total P in the sediments in Han River, Seoul, Korea, ranged from 0.58–1.15 g · kg^{-1}. The Han River, the largest river in Korea, is the primary water source for more than 20 million people in Seoul and the surrounding area. It starts in north-east Kangwon-Do and flows to the Yellow Sea through Seoul. The river is 469.7 km long [11].

The Swale River in UK drains a rural catchment with no major urban and industrial areas, and the total phosphorus content of fluvial sediment is generally within the range 0.50–1.50 g · kg^{-1}. Swale River (1363 km^2) drains a largely rural (moorland and agricultural) area. This river is a relatively unpolluted one along its entire length, and drains a predominantly rural catchment with a low population density [12].

Analysis of the main sources of phosphorus within the catchment of upper Narew River revealed hypothesized may be the sewage discharges – mostly domestic and farm (Table 1) – from small towns, cities and above all from Bialystok city (industrial wastewaters in part) localized within the catchment. The sewage treatment plants operate in these places, but periodically they are not able to remove sufficient amounts of phosphorus and other redundant components from wastewaters.

Studies revealed following average contents of phosphorus in the bottom sediments of Narew River – 1.31 g · kg^{-1} d.m., Supraśl – 0.33 g · kg^{-1} d.m., Narewka – 0.40 g · kg^{-1} d.m., Orlanka – 0.24 g · kg^{-1} d.m., and Nereśl – 0.36 g · kg^{-1} d.m. In each of these cases, the influences of point sources of phosphorus forms, mostly related to

Table 2

Phosphorus content in bottom sediments of rivers within upper Narew River catchment

River	Localization of measurement point	[g · kg^{-1}]
Narew	1. Bondary	0.40
	2. Narew	0.70
	3. Ploski	3.50
	4. Doktorce	0.85
	5. Uhowo	0.20
	6. Bokiny	0.20
	7. Rzedziany	0.55
	8. Zlotoria	1.10
	9. Siekierki	1.65
	10. Tykocin	3.90
	Arithmetic mean	1.31
	SD	1.34
Suprasl	1. Topolany	0.30
	2. Michalowo	0.30
	3. Grodek	0.25
	4. Suprasl	0.35
	5. Nowodworce	0.25
	6. Fasty	0.55
	Arithmetic mean	0.33
	SD	0.11
Narewka	1. Bialowieza	0.30
	2. Narewka	0.75
	3. Lewkowo	0.30
	4. Eliaszuki	0.25
	Arithmetic mean	0.40
	SD	0,24
Orlanka	1. Orla	0.25
	2. Krzywa	0.25
	3. Kotly	0.25
	4. Chraboly	0.20
	Arithmetic mean	0.24
	SD	0.03
Neresl	1. Czechowizna	0.25
	2. Bajki Zalesie	0.55
	3. Piaski	0.20
	4. Fasty	0.45
	Arithmetic mean	0.36
	SD	0.17

Table 2 contd.

River	[g · kg^{-1}]
Jaskranka	0.20
Czarna	0.50
Ruda	0.75
Rudnia	0.40
Czaplinianka	0.30
Loknica	0.20
Awissa	0.40
Mienka	0.25
Turosnianka	0.50
Horodnianka	0.25
Krzywczanka	0.20
Malynka	0.40
Strabelka	0.10

sewage treatment plants functioning within the catchment area, can be found. Spatial distribution of phosphorus contents in bottom sediments of Narew River (points 1, 2 and 3) (Fig. 1, Table 1) can also indicate the impact of the water reservoir Siemianówka. In the summer, during an intense algal bloom, the reservoir becomes a major source of phosphorus to the waters of Narew River.

The impact of Biała River that transports contaminants from the city of Bialystok to Supraśl River is also prominent (point 6 – Fasty 0.55 g · kg^{-1} d.m.) (Fig. 1, Table 2). The effect of Bialowieza and Narewka River (municipal waste treatment plants) on the amount of phosphorus in bottom sediments of Narewka River can be also noted (point 2, 0.75 g · kg^{-1} d.m.). Considering the group of small rivers, the largest concentrations of phosphorus were recorded in sediments of Ruda River (0.75 g · kg^{-1} d.m.), while the lowest levels of this element – in bottom sediments of Strabelka River (0.10 g · kg^{-1} d.m.). The Geochemical Atlas of Poland [13] provides details of the descriptive statistics for the group of 993 analyzed sediment samples collected from different lakes. The phosphorus content in these samples ranged from < 0.05 g · kg^{-1} to 8.01 g · kg^{-1} d.m., and the arithmetic mean value amounted to 0.28 g · kg^{-1} d.m. It can be concluded that the quantity of phosphorus in bottom sediments of the upper Narew River catchment is not large, but slightly increased probably due to anthropogenic pressure.

The studies and calculations show that the greatest impact on the amount of phosphorus in the bottom sediments was exerted by: urbanized areas and the volume of sewage ($r_{0.05}$ = 0.45 and $r_{0.05}$ = 0.40, respectively) (Table 3). Urbanized areas, length of river and catchment area shape the volume of sewage discharged into the rivers, which was expressed by means of Spearman coefficients $r_{0.05}$ = 0,57, $r_{0.05}$ = 0.48, $r_{0.05}$ = 0.61, respectively. In part, that confirmed the dependence of phosphorus concentrations on the percentage of urbanized areas surface in the upper Narew River catchment. Forests localized within the catchment area have little influence on the quantities of phosphorus in bottom sediments of upper Narew River catchment ($r_{0.05}$ = 0.20).

Table 3

Spearman correlation coefficients (r) for achieved dependencies ($p < 0.05$)

Component	Urbanized areas [%]	Forests [%]	Length of river [km]	Catchment area [km^2]	Amount of domestic sewage discharged into the rivers [m$^3 \cdot$ d^{-1}]
Phosphorus in bottom sediments [%]	0.45	0.20	n.s.*	0.25	0.40
Amount of domestic sewage discharged into the rivers [m$^3 \cdot$ d^{-1}]	0.57	n.s.	0.48	0.61	—

* n.s. – not significant.

The studies phosphorus in bottom sediments of rivers are conducted less frequently in comparison with deposits in lakes, thus a smaller amount of scientific publications dealing with the phosphorus in river sediments. However, studies of phosphorus in bottom sediments of rivers should be carried out more frequently due to the large number of point sources of this nutrient, usually in the form of sewage treatment plants. Bottom sediments of rivers can become, under certain conditions, a secondary source of phosphorus to the river waters, like point and surface sources.

Conclusions

1. The highest contents of phosphorus in bottom sediments were found in Narew River (1.31 g $\cdot$ kg^{-1} d.m.), while the lowest in Strabelka River (0.10 g $\cdot$ kg^{-1} d.m.).
2. Comparison with other research revealed that studied sediments were characterized by a typical content of phosphorus, and locally increased amounts of this element are the result of limited, however still existing anthropogenic pressure.
3. The study demonstrates a relationship between phosphorus in bottom sediments and the nature of particular rivers catchments, including the amount of sewage discharged into these rivers.
4. Method of management and morphology of the catchment determine the quantitative migration of phosphorus into the surface waters and then to the bottom sediments. These sediments may contribute to additional, secondary enrichment of waters with phosphorus, which should be one of the pretexts for the continuous quantitative monitoring of the element in the bottom sediments of rivers.

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FOSFOR W OSADACH DENNYCH RZEK Z OBSZARU ZLEWNI GÓRNEJ NARWI

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Abstrakt: Celem pracy było określenie zawartości fosforu w osadach dennych rzek z obszaru zlewni górnej Narwi. W pracy analizowano zmiany zawartości fosforu w osadach na tle przestrzennego rozkładu punktowych źródeł tego składnika oraz zidentyfikowano główne czynniki jego wzbogacania związane z morfometrią i zagospodarowaniem zlewni. Badaniami objęto rzekę Narew w 10 przekrojach pomiarowych na odcinku Bondary – Tykocin oraz rzekę Supraśl, na której wytypowano 6 punktów pomiarowych. W czasie doboru miejsc pobierania próbek osadów dennych za główne kryterium przyjęto obecność ognisk wzbogacania środowiska wodnego w fosfor, głównie oczyszczalni ścieków. Do analiz pobierano również próbki z 17 mniejszych i większych dopływów Narwi. Największe zawartości fosforu wykazano w osadach dennych Narwi (1,31 g $\cdot$ kg^{-1} s.m.), a najmniejsze w osadach Strabelki (0,10 g $\cdot$ kg^{-1} s.m.). Porównanie z innymi badaniami wykazało, że badane osady charakteryzują się typową zawartością fosforu, a lokalnie zwiększone ilości tego składnika są wynikiem ograniczonej wprawdzie, ale istniejącej presji antropogennej. W pracy wykazano, że istnieje zależność zawartości fosforu w osadach dennych od charakteru zlewni poszczególnych rzek, w tym od ilości ścieków odprowadzanych do tych rzek.

Słowa kluczowe: fosfor, osady denne, rzeki, ścieki

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CONCENTRATION OF CERTAIN TOXIC SUBSTANCES IN SEEPAGE WATER IN RELATION TO DISTANCE FROM SHEEPFOLD

ZAWARTOŚĆ NIEKTÓRYCH SUBSTANCJI TOKSYCZNYCH W WODACH ODCIEKOWYCH W ZALEŻNOŚCI OD ODLEGŁOŚCI KOSZARU OWCZEGO

Abstract: The study was conducted in the mountain terrain on a pasture, where sheep grazing took place. The soil of this area was brown, classified with texture as loamy sand. Prevailing species in the turf were red fescue (*Festuca rubra*) and common bent-grass (*Agrostis capillaris*). The aim of the study was to determine levels of toxic substances in water moving downhill out of a sheepfold along a 6ş slope. In spring 2009 plastic cylinders 50 cm in length and 3 cm in diameter were inserted vertically into soil: in the pasture above the fold (control object), then inside the fold and beneath its surface as three replications along the slope placed 3 m apart in order to collect seepage water. The farthest migration among the whole of analysed elements was distinctive for nitrogen NH_4-N + NO_3-N. As regards the other elements, they had the highest concentration in water from within a sheepfold. Their migration out of folding place was minimal. The highest nitrogen N-NO_3 + N-NH_4 content was found in seepage water from the cylinder fixed into the fold measuring 11.75 mg $\cdot$ dm^{-3} at the first sampling and 9.07 mg $\cdot$ dm^{-3} at the second one. With increasing distance out of the sheepfold this value was decreasing and at 9 m below it was reduced to 6.10 mg $\cdot$ dm^{-3} and 6.76 mg $\cdot$ dm^{-3}, respectively, for the two successive samplings.

Keywords: sheep grazing, sheepfold, seepage water, toxic substances

Introduction

The primary system of sheep maintenance in piedmont and mountain areas is pasturing. Sheep ability to bite plants at minimum height as well as their relatively low demands for green fodder quality are generally known [1, 2]. Such a way of gathering

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herbage crop contributes to sustaining biodiversity between species and results in numerous positive changes within the soil [3]. Furthermore, owing to sheep-folding manure one will obtain higher production of the fodder, which is enriched with macro- and micronutrients required by animals grazed [4–6]. Sheep staying day-and-night in a pasture for the growing season have a beneficial impact on matter circulation in the environment. Another feature of sheep grazing is the fact that animals are hurdled for the time of milking and for night. Concentration of biogenic elements left by sheep in folding sites is high [6, 7]. There is a risk that biogenic elements would escape from a sheepfold with surface runoff or permeate into watercourses, especially in places where sheepfold locations are extremely inclined and/or receive abundant rainfall.

The aim of this study was to determine levels of toxic substances in water moving downhill out of a sheepfold. It was assumed that the concentration of chemicals in water seepage collected along the slope below the sheepfold would change.

Material and methods

The study was conducted in a mountain pasture underneath the Jaworzyna summit near Krynica, where sheep grazing took place (N 49°24′57.38″, E 20°55′32.26″). An investigated area with a 6° slope was situated at an elevation of 613 m a.s.l. The soil prevailing in this pasture was brown, classified with texture as loamy sand. Its chemical properties were as follows: pH_{KCl} – 3.8; total N – 3.5 $g \cdot kg^{-1}$; organic matter – 50.6 $g \cdot kg^{-1}$; available P, K and Mg – 10.9, 75.5 and 76.0 $mg \cdot kg^{-1}$, respectively. Weather conditions in the area of the study are presented in Table 1.

Table 1

Mean daily temperature of air and monthly sum of precipitations during study period

Months	Mean daily air temperature [°C]		Monthly sum of precipitation [mm]	
	2009	2010	2009	2010
January	–4.9	–6.3	23.6	21.6
February	–3.1	–3.3	30.6	25.8
March	0.0	0.4	101.4	40.0
April	8.7	6.2	13.0	83.2
May	10.8	11.1	104.0	194.6
June	13.5	14.5	194.0	203.8
July	17.0	17.5	118.8	156.2
August	15.8	16.3	115.5	118.9
September	12.6	9.9	41.7	198.8
October	5.5	3.5	78.1	17.9
November	2.9	4.9	71.7	30.9
December	–2.5	–6.2	35.8	40.4
April – September	13.1	12.6	587	955.5
January – December	6.4	5.7	928	1132

Predominant species in the turf were red fescue (*Festuca rubra*) and common bent-grass (*Agrostis capillaris*). Sheep left over the fold surface 4790 kg faeces and 3710 kg urine per hectare.

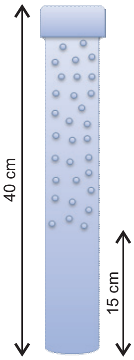

Fig. 1. Diagram of cylinder to collect seepage water

In spring 2009 plastic cylinders 50 cm in length and 3 cm in diameter (Fig. 1) were inserted vertically into soil: in the pasture above the fold (control object), then inside the fold and beneath its surface as three replications along the slope placed 3 m apart (Fig. 2).

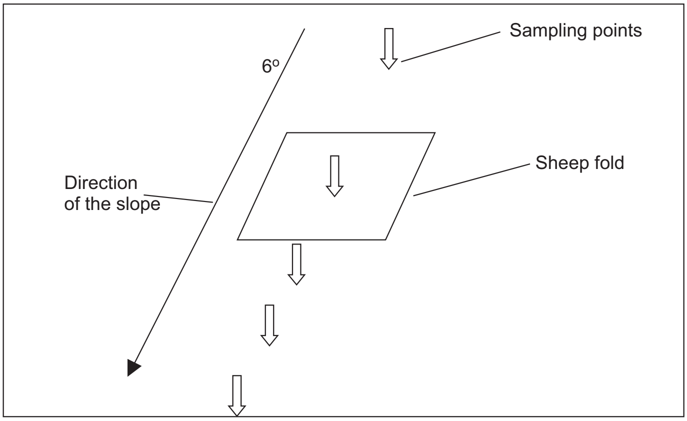

Fig. 2. Scheme of slope direction and location of sampling points

The walls of each cylinder had apertures in a range between 15 and 50 cm of height, where water may enter and accumulate within a cylinder (up to 15 cm of height). Collected water from each cylinder (one month and one year after folding) was used twice to estimate levels of the following elements: NH_4-N + NO_3-N, Cd, Pb, Cr and Ni. Nitrogen content was determined with a microchip photometer LF-205, while the other elements with the aid of the ICP-AES technique. Obtained data underwent statistical appraisal including one-way analysis of variance and LSD test at a significance level of $\alpha < 0.05$ with Statistica 7 software.

Results

The highest level of nitrogen, as NH_4-N + NO_3-N, was found in the first-year sample of drained water from the cylinder fixed in sheep manured surface (Table 2). At the time nitrogen content in water obtained from the sites of 3 and 6 m down from the sheepfold was 25 % lower than in water from the folding object.

Table 2

Levels of NH_4-N + NO_3-N, Pb, Cd, Ni, Cr in seepage water for different sites of sampling

Site of sampling		NH_4-N + NO_3-N	Pb	Cd	Ni	Cr
		[mg · dm^{-3}]	[mg · dm^{-3}]			
Date of sampling 02.06.2009						
Control, at 20 m above sheepfold		6.42 a*	1.83 c	0.90 a	9.14 a	11.03 a
Sheepfold		11.75 c	4.80 b	3.50 b	12.20 b	15.40 b
Below sheepfold	at 3 m	8.59 b	2.90 b	0.80 a	10.50 ab	14.20 b
	at 6 m	8.81 b	3.40 b	0.90 a	9.40 a	12.40 a
	at 9 m	6.10 a	3.60 b	1.00 a	10.20 a	12.80 a
Date of sampling 15.05.2010						
Control, at 20 m above sheepfold		5.87 a	1.72 a	0.64 a	8.82 a	10.42 a
Sheepfold		9.07 c	4.50 b	2.60 b	10.10 b	13.90 b
Below sheepfold	at 3 m	7.45 b	1.30 a	0.60 a	7.80 a	11.30 a
	at 6 m	7.92 b	1.10 a	0.70 a	8.90 a	12.70 a
	at 9 m	6.76 a	1.00 a	0.50 a	7.20 a	10.60 a

* Letters a, b, c indicate homogenous groups according to LSD test, $\alpha < 0.05$.

Water collected at 9 m below the sheepfold contained 6.10 mg · dm^{-3}, which is 49 % less than the value recorded for the fold, although quite similar to the control object. In the next-spring sampling water nitrogen level from the manured object was 9.07 mg · dm^{-3} being 33 % lower than at the prior time. Also at the sites 3 and 6 m from the fold nitrogen content was 10–15 % lower to earlier values for the same objects. At the 9 m distance from the fold a level of NH_4-N + NO_3-N in seepage water was 10 % higher when set beside the previous-year sampling, even though the difference to the control object was not significant statistically.

Lead concentration in the first-year examination of seepage water taken in the sheepfold reached 4.80 mg · dm^{-3} and was 2.5 times as great as the control one, whereas in comparison with the other objects this result was 30–40 % higher. In the successive sampling lead concentration in water drained at each investigated object decreased, especially for the three ones below the fold, in which a range of such reduction fell between 65 and 72 %.

Cadmium level at the first-year sampling of water from the sheep folding area was almost quadrupled when set beside the other object measures ranging from 0.80 to 1.0 mg · dm^{-3}. At the next-year sampling the concentration of cadmium in water taken from each object was 25–50 % lower. The differences in Cd level in water sampled outside the fold were found not significant.

Changes in nickel concentration in water between two yearly samplings as well as differences among objects outside the fold within the same time of sampling were small and ranged from 1.2 to 2.9 mg · dm^{-3}. The relative measure of the differences falls within the range of 12 to 29 %. The highest Ni level was found in water taken in the sheepfold at the first-year sampling; then after a year its concentration in water from the same object was 17 % lower.

The highest chromium level was found at the first-year sampling in water taken from cylinders fixed into the fold and the site 3 m below, and a difference between those objects was not significant. In the other objects Cr level averaged out to 15 % lower measure. After a year chromium concentration was reduced 5 to 20 % except from the object at 6 m below the fold, where a 2% increase was recorded.

Discussion

From the obtained results one must state unequivocally that manuring with the use of sheepfolds is a point source of pollution. At employing them water environment deteriorates due to contamination, in particular with nitrogen NH_4-N + NO_3-N, both inside sheepfolds and in underneath areas. This is evidence for fast migration of nitrogen compounds with seepage water. Their rapid relocation is confirmed by the works of Barszczewski and Sapek [8] and Barszczewski and Paluch [9]. On the basis of their NH_4-N and NO_3-N content the water analysed in the study was classified as falling outside the II class, where no further limits are established by the Regulation of the Minister of Environment dated 20 August 2008 [10]. Great differences in lead and cadmium levels among the sites pointed out their slow migration and high concentration in sheep excreta. Also nickel and chromium moved with seepage water at a rather low speed, however, in contrast to the prior mentioned elements, their concentration in sheep excreta was minor. The study demonstrated for each examined toxic substance that its concentration in seepage water was reduced with growing distance from the manured place and with duration of time. This is clearly evident for lead and cadmium above all and could be explained by the fact that turfs, owing to their function as a biological filter, are able to absorb these elements and to inhibit their spread in environment [11]. To sum up, from the results of previous and current investigation one can conclude that folding would be a good method of fertilisation, although its economical and environmental effect depends on time length spend in fold by sheep, stock density and distance from watercourses.

Conclusions

1. Levels of nitrogen, lead and cadmium in seepage water were excessive, concentration of nickel and chromium were increased as well.

2. Nitrogen and lead were migrating very fast out of sheepfold with seepage water.

3. After one year nitrogen concentration in seepage water outside fold remained high, while lead, cadmium, nickel and chromium levels was similar to control.

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ZAWARTOŚĆ NIEKTÓRYCH SUBSTANCJI TOKSYCZNYCH W WODACH ODCIEKOWYCH W ZALEŻNOŚCI OD ODLEGŁOŚCI KOSZARU OWCZEGO

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Abstrakt: Badania zrealizowano na pastwisku w rejonie górskim, na którym prowadzono kulturowy wypas owiec. Na tym terenie występowała gleba brunatna o składzie granulometrycznym piasku gliniastego. Dominującymi gatunkami w runi były kostrzewa czerwona (*Festuca rubra*) i mietlica pospolita (*Agrostis capillaris*). Celem badań było określenie poziomu substancji toksycznych w wodzie przemieszczającej się z koszaru owczego wzdłuż stoku o nachyleniu 6^o.

Wiosną 2009 r. na pastwisku powyżej koszaru (obiekt kontrolny), na powierzchni koszarowanej i w trzech punktach poniżej koszaru, w odległościach co 3 m, umieszczono pionowo w glebie plastikowe cylindry o średnicy 3 cm i długości 50 cm. Na ściankach cylindrów na wysokości od 15 do 50 cm były wykonane otwory, przez które przenikała przesiąkająca woda i gromadziła się w ich dolnej części (od 0 do 15 cm). W zgromadzonej w cylindrach wodzie oznaczono dwukrotnie w 30 dniu po koszarzeniu i w 347 dniu (wiosną

2010 r.) zawartość następujących składników: N-NO$_3$ + N-NH$_4$, Cd, Pb, Cr i Ni. Zawartość azotu oznaczono fotometrem mikroprocesorowym LF-205, a stężenie pozostałych składników metodą ICP-EAS.

Spośród analizowanych składników azot (N-NO$_3$ + N-NH$_4$) w największym stopniu ulegał przemieszczaniu. Natomiast największe stężenie pozostałych składników występowało w wodzie w obrębie koszaru. Ich przemieszczanie poza koszar było znikome. Największą zawartość azotu N-NO$_3$ + N-NH$_4$ charakteryzowała się woda odciekowa zgromadzona w cylindrze umieszczonym wewnątrz koszaru. W pierwszym terminie zawartość ta wynosiła 11,75 mg · dm^{-3}, a w drugim 9,07 mg · dm^{-3}. W miarę oddalania się od koszaru stężenie tego składnika zmniejszało się i w odległości 9 m od koszaru wynosiło w pierwszym roku 6,10 mg · dm^{-3}, a w drugim 6,76 mg · dm^{-3}.

Słowa kluczowe: wypasanie owiec, koszar, wody odciekowe, substancje toksyczne

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ELECTROCOAGULATION OF MODEL WASTEWATER USING IRON ELECTRODES

ELEKTROKOAGULACJA ŚCIEKÓW MODELOWYCH NA ELEKTRODACH ŻELAZNYCH

Abstract: This paper presents the results of electrocoagulation of model wastewater using iron electrodes under laboratory conditions. The investigated wastewater was susceptible to electrolytic treatment, and the model system supported the performance of analyses in seven replications, generating a database for reliable statistical and mathematical processing. Wastewater was treated by chronopotentiometric electrocoagulation in a static system at constant current intensity $I = 0.3$ A. Changes in supply voltage for $I = \text{const}$ were registered over time. Changes in pH, turbidity, chemical oxygen demand (COD), suspended solids and total phosphorus concentrations in the treated wastewater were determined. A new method for determining the optimal dosage of the iron electrocoagulant was proposed by relying on the third degree polynomial function rather than the parabolic equation. The proposed method, justified theoretically and demonstrated practically, enabled precise determination of the electrocoagulant dose. An increase in the electrocoagulant dose increased the share of sweep electrocoagulation in the wastewater treatment process.

Keywords: model wastewater, dose of iron electrocoagulant

Wastewater is popularly treated with the involvement of mechanical and biological methods. Their effectiveness may be limited, therefore supplementary treatment methods are often deployed. One of such methods involves chemical coagulation which supports the biological treatment of wastewater. Chemical coagulation is used to remove excess orthophosphate ions from industrial and municipal effluents with the application of the following reagents: aluminum and iron sulfates, iron(III) chloride, other iron coagulants [1] and polyaluminum chloride (PAC) [2]. The results generated by treatment models [3] and simulations [4, 5] continue to expand our knowledge about the chemical coagulation process.

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Electrocoagulation poses an alternative to chemical coagulation in the treatment of water and effluents. Electrocoagulation methods generally involve iron or aluminum anodes that undergo electrolytic dissolution. Iron and aluminum ions are introduced to the processed water or effluent where they act as electrocoagulants. In the process of oxygen cathodic polarization, the introduction of coagulating Fe^{2+} ions which undergo oxidation to Fe^{3+} increases the system's pH [6], whereas conventional chemical coagulation always lowers pH due to the hydrolysis of Fe^{3+} cations (PIX) [7]. In chemically coagulated and electrocoagulated wastewater, Fe^{3+} cations create positive micelles $\{Fe(OH)_3\}$ that act as colloidal sorbents [8] for wastewater pollutants such as suspended solids, phosphorus compounds and substances responsible for the COD load.

In markets characterized by cheap energy and high cost of transporting chemicals, electrocoagulation poses a vital alternative to chemical coagulation since iron electrodes are much lighter than coagulating substances, *eg* PIX. Electrocoagulation requires simple equipment and is easy to operate. The addition of sea water, which is characterized by a high content of NaCl as the conductor of electricity, to wastewater or water [9,10] significantly lowers electricity consumption during electrocoagulation. Chloride compounds, the by-products of the process, additionally disinfect the treated effluents.

The experiment described in this study supported the development of a new method for the quantitative interpretation of the electrocoagulation process and the determination of the optimal iron electrocoagulant dose. It also attempted to explain the mechanism of treating model wastewater by electrocoagulation using iron electrodes in a static system.

Metods

The chronopotentiometric electrocoagulation process was carried out at constant current intensity (I = const) with the use of iron electrodes in a device shown in Fig. 1.

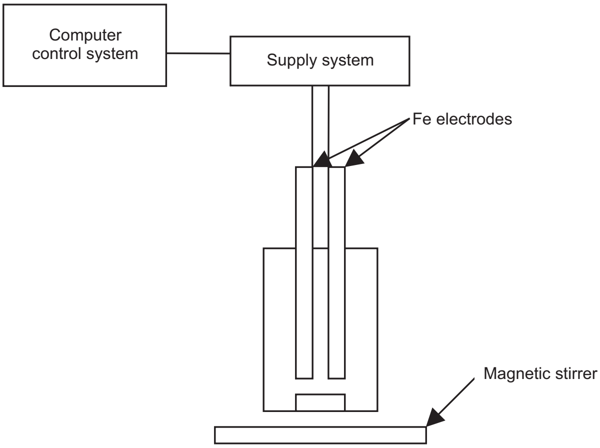

Fig. 1. Laboratory device for static electrocoagulation of wastewater

100 cm^3 of freshly prepared model wastewater with a phosphate buffer was poured into six laboratory beakers. Saturated NaCl solution was added to each beaker in quantities (usually 11 drops) that increased specific conductivity to $\kappa \approx 4$ mS. To ensure the equivalence of wastewater electrocoagulation, the anticipated electrocoagulant dose m was input each time into Faraday's equation

$$m = k \cdot I \cdot t,$$

where: m – weight of the iron electrocoagulant in grams,
k – electrochemical gram equivalent of Fe(II); $k = 56/2 = 28$ g,
I – electric current in amperes,
t – and the planned electrocoagulation time was determined at $I = 0.3$ A = const, electrolysis time in seconds.

Current I was kept constant at 0.3 A, and higher doses of electrocoagulant required longer electrocoagulation time t. The iron electrocoagulant was dosed as follows:

- beaker 1 = 512 s electrolysis,
- beaker 2 = 768 s,
- beaker 3 = 1024 s, etc.

Electrocoagulation was carried out with the use of two iron electrodes measuring $100 \cdot 10 \cdot 1$ mm each. The electrodes were immersed at a depth of 5 cm, with a precise spacing of 1 cm, in 100 cm^3 beakers containing model wastewater. Wastewater was continuously stirred with an electromagnetic stirrer. Treatment took place at constant current of $I = 0.3$ A and registered voltage V. Every 256 s, the control system automatically changed the direction of current flow on the electrodes to enable cathode self-cleaning [11]. A contaminated cathode was thus transformed into a soluble anode, and it was purified by anode dissolution. The entire process was controlled by a computer. A unique hardware and software system had been designed and built for the needs of the experiment.

After electrolysis, samples were collected from the supernatant layer, and the following wastewater parameters were determined after 30 min of sedimentation with the application of standard HACH methods [12]: pH, COD, total phosphorus, turbidity and suspended solids concentrations. Electrocoagulation was performed in seven replications, and the two highest and the two lowest values were rejected. The remaining three values were used to compute the mean value and the standard deviation (SD). The results were presented in graphic form.

Results

The changes in supply voltage V for constant $I = 0.3$ A were registered over time t. The average values of function $V = f(t)$ are shown in Fig 2.

A clear change in current direction can be observed every 256 s. This value guarantees electrode (cathode) self-cleaning and it minimizes polarization loss, therefore it was adopted as the optimum parameter for electrocoagulation in model systems [11].

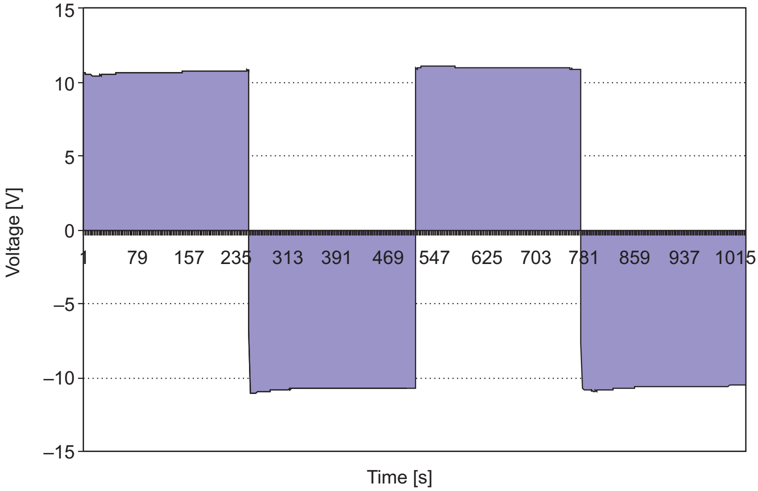

Fig. 2. Changes in voltage over time producing I = const = 0.3 A

During electrolysis time of 256 s, voltage did not exceed 11 V, + or –, respectively. In semi-technical and industrial tests investigating natural wastewater, the above data would support the full determination of electrocoagulation parameters, including electric power, power consumption, etc.

The changes in wastewater pH during electrocoagulation with the use of iron electrodes are presented in Fig. 3. The electrocoagulation process always increased the pH of treated wastewater to around 9.2. One of the reasons for the pH increase during electrocoagulation is hydrogen ion secretion resulting from water reduction at the cathode:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \tag{1}$$

The electrocoagulation process with the use of iron electrodes, at pH > 7, leads to the following reactions at the phase boundary:

$$Fe^o - 2e^- \longrightarrow Fe^{2+} \tag{2}$$

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \tag{3}$$

$$Fe^{2+} - e^- \longrightarrow Fe^{3+} \tag{4}$$

$$Fe(OH)_2 + OH^- - e \longrightarrow Fe(OH)_3 \tag{5}$$

Depending on wastewater pH during electrocoagulation, iron may form the following ions:

$$Fe(OH)^{2+},\ Fe(OH)_4^-,\ Fe_2(OH)_2^{4+},\ Fe(H_2O)_4(OH)_2^+,$$

subsequently converted to $Fe(OH)_3$ [6]. The type of the resulting ions and wastewater pH may significantly influence treatment effectiveness.

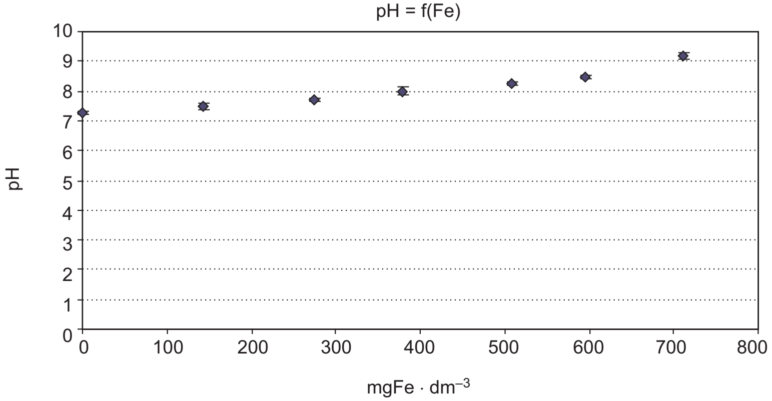

Fig. 3. Changes in wastewater pH

In experiments involving iron electrodes, iron(II) ions were generated into the system, and they were partially oxidized to iron(III). The above was demonstrated by the color of the treated wastewater and supernatant which changed from grayish green to reddish brown. At high pH and in aerobic conditions, Fe^{2+} ions and their hydroxyl complexes are easily converted to $Fe(OH)_3$ and FeOOH, the co-products of the process. Those co-products may be transformed into hydrogenated iron(III) hydroxy species in the following reaction [13]:

$$Fe(OH)_{3(s)} + \alpha\text{-}FeOOH_{(s)} \longrightarrow H_{(aq)}(OH)OFe_{(s)} \tag{6}$$

The resulting species are electrically neutral, and they are unable to destabilize negatively charged wastewater pollutants. Owing to their surface charge, they can absorb pollutants on the surface, scavenge them and form complexes with those impurities.

The removal of suspended solids from wastewater coagulated with the use of an iron electrocoagulant is presented in Fig. 4. In the above third-degree polynomial curve, the

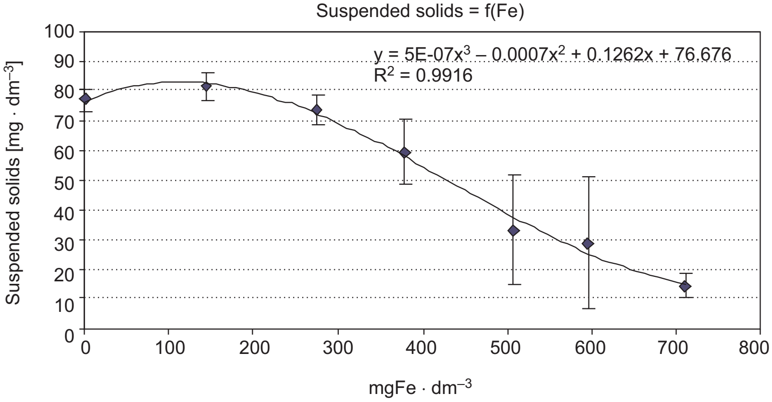

Fig. 4. Removal of suspended solids from wastewater

point of inflection is determined at an electrocoagulant dose of 550 mgFe · dm^{-3}. The effectiveness of the applied mathematical model is demonstrated by the high value of the coefficient of determination $R^2 = 0.9916$. Significant standard deviation values could be attributed to very long flocculation times and the resulting difficulty in collecting water samples above the sediment layer. A small portion of flocs was always sampled together with a specimen of treated waste.

The most effective dose that removed nearly 81 % of suspended solids was around 710 mgFe · dm^{-3}. A much lower dose of approximately 590 mgFe · dm^{-3} resulted in 63 % efficiency, which is a relatively satisfactory result in the initial phase of chemical wastewater treatment. The use of PIX in similar conditions reduced suspended solid concentrations by 63 % [8].

Treatment effectiveness is largely determined by the form of ions which emerge as "primary" ions in the electrocoagulation system. Based on the Pourbiax diagram [14], it can be assumed that the predominant monomeric forms of iron in the experiment were colloidal $Fe(OH)_3$ and $Fe(OH)_4^-$ ions. Those ions do not destabilize negatively charged pollutants, and they merely bridge positively charged impurities. It can be assumed that at low initial doses of the electrocoagulant, the predominant process during wastewater treatment is sorption on colloidal micelles of iron hydroxide, whereas the share of sweep electrocoagulation increases gradually at higher electrocoagulant doses [15].

The removal of turbidity from model wastewater coagulated with the use of iron electrocoagulant is presented in Fig. 5. The curve shows a high degree of similarity to function *Suspended solids = f(Fe)*. The noted similarity validates the control function, *ie* the correlation between wastewater turbidity and suspended solids. Similarly to the removal of suspended solids, the most effective dose of around 710 mgFe · dm^{-3} removed turbidity in nearly 62 %. The highest dose of 710 mgFe · dm^{-3} was only 2 % more efficient than the dose of 590 mgFe · dm^{-3}.

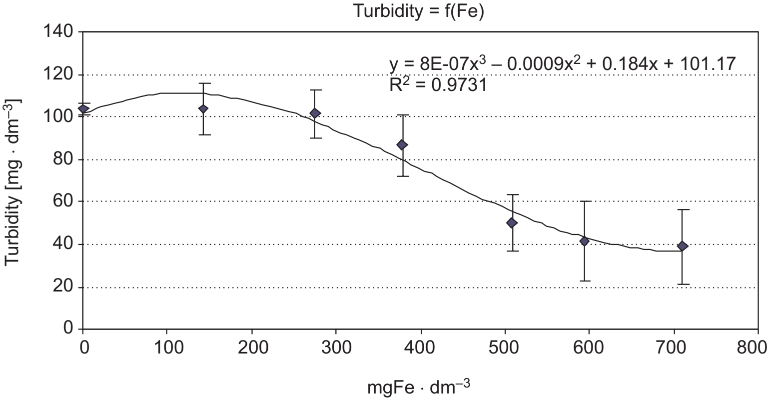

Fig. 5. Removal of wastewater turbidity

Such high coagulant doses resulted probably from the high pH levels of treated wastewater. Similarly as with suspended solids, an increase in pH after electrocoagulation caused a decrease in the sorption on colloidal micelles of iron hydroxide and an increase in the sweep of pollutants as a result of their direct contact with sedimenting flocs of iron(II) and iron(III) hydroxides.

The third-degree polynomial curve in Fig. 6 illustrates the removal of phosphorus compounds from wastewater coagulated with an iron electrocoagulant. Significant standard deviation values can probably be attributed to the slow sedimentation of iron hydroxide flocs. Due to sedimentation (or flotation), not all flocs with absorbed pollutants are removed from treated wastewater, and they may be sampled together with the analytical specimen. Samples are rarely filtered before analysis for practical reasons. Relatively high standard deviation values were reported as a result of the sedimentation procedure. Despite the above, the curve shown in Fig. 6 is characterized by a high coefficient of determination $R^2 = 0.9792$, thus further validating the choice of the applied mathematical model.

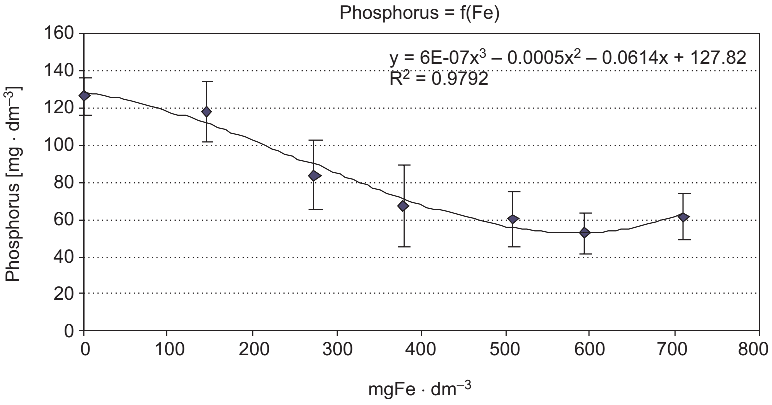

Fig. 6. Removal of phosphorus compounds from wastewater

In the analyzed curve, the point of inflection was determined at a electrocoagulant dose of approximately 380 mgFe · dm^{-3}, which was much lower than that in suspended solids and turbidity diagrams. Unlike in those diagrams, a dose increase to 710 mgFe · dm^{-3} in the discussed curve did not lead to changes in phosphorus concentrations in treated wastewater. It could be expected that a further increase in the electrocoagulant dose would inhibit the sorption-coagulation process, leading to an insignificant destabilization (peptization) of sludge and a drop in phosphorus concentrations above the sludge.

The highest of the three applied doses were marked by similar phosphorus removal efficiency in the range of 51–58 %. Electrocoagulation with iron electrodes was characterized by phosphorus removal efficiency similar to that delivered by PIX [8]. The differences in the doses of chemical coagulants and electrocoagulants result from the effect of the system's pH and the direction of changes in pH on the treatment process. The pH of wastewater significantly influences the structure of active ionic forms of iron, and treatment effectiveness is largely determined by the "primary" forms. In this experiment, the lowest dose of the iron electrocoagulant raised pH to approximately 7.5 (Fig. 3), and a further increase in electrocoagulant doses resulted in pH > 9. At such high pH levels, the system is characterized by a predominance of monomeric iron species [6], *ie* colloidal iron hydroxides and $Fe(OH)_4^-$ ions. The above ions are unable to destabilize negatively charged phosphates. It should be noted that a Fe : P molar ratio higher than 1 : 3, which guarantees the removal of phosphorus from wastewater, rules out a simple precipitation reaction, such as: $Fe_3(PO_4)_2\downarrow$, $FePO_4\downarrow$, $(FeOH)_3(PO_4)_2\downarrow$, $(FeOH)_3PO_4\downarrow$, as a process of removing phosphorus from wastewater by electrocoagulation with the use of iron electrodes.

The removal of substances responsible for the COD load from model wastewater coagulated with the use of iron electrocoagulant is presented in Fig. 7. The COD curve is characterized by a high coefficient of determination $R^2 = 0.9916$ and low standard deviation values. The above confirms the analyzed wastewater's susceptibility to electrolytic treatment and high goodness of fit of the applied mathematical model (third degree polynomial) for the resulting experimental data.

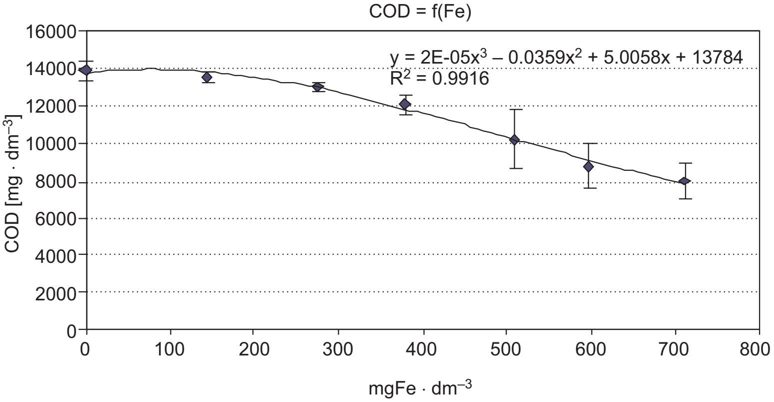

Fig. 7. Removal of substances responsible for the COD load

The most satisfactory results were reported for the highest dose of 710 mgFe · dm^{-3} which removed 43 % of substances responsible for the COD load. The noted results are superior to PIX [8], but the required dose is 1.5-fold higher. The higher efficiency of the iron electrocoagulant than PIX resulted from differences in the system's pH and the direction of changes in pH values during wastewater treatment.

Experimental conditions supported sweep coagulation. Higher electrocoagulant doses raised pH which, in turn, increased the share of sweep coagulation. In chemical coagulation, an increase in chemical coagulant doses lowered the system's pH and contributed to the destabilization of wastewater colloids. The drop in pH was also accompanied by the risk of sludge peptization. The above attests to the parabolic character of changes in suspended solid concentrations, turbidity, phosphorus concentrations and COD levels as a function of the coagulant dose. High pH levels during electrocoagulation significantly minimize the risk of sludge peptization, suggesting that the third-degree polynomial curve better fits electrocoagulation data than a parabola.

The observed changes in turbidity, suspended solids and phosphorus compound concentrations and substances responsible for the COD load in electrocoagulated wastewater indicate that experimental conditions supported sweep coagulation. Growing pH during treatment and a high final pH prevented the generation of effective iron cations that ensure high treatment effectiveness at the stage of latent and slow coagulation. The iron species produced in the presence of excess electrocoagulant ions in an alkaline environment supported:

a) sorption of substances responsible for the COD load on the surface of colloidal iron hydroxide,

b) bridging of positively charged impurities with the involvement of, for example $Fe(OH)_4^-$,

c) sweeping of neutral as well as positively and negatively charged impurities that remained in direct contact with sedimenting iron hydroxide flocs.

Conclusions

The investigated model wastewater was susceptible to electrocoagulation treatment with the use of iron electrodes. In every experimental area, turbidity removal values fully validated the results reported in respect of suspended solids removal. The third degree polynomial method was used to plot curves showing changes in COD, total phosphorus concentrations, turbidity and suspended solids concentrations during wastewater treatment and to calculate the relevant electrocoagulant doses. Every increase in the iron electrocoagulant dose raised the pH of treated wastewater and minimized the probability of destabilization of negatively charged wastewater colloids. The share of sweep coagulation in the treatment process increased with a rise in the applied electrocoagulant dose. The noted values of the Fe : P molar ratio suggest that phosphorus removal from the treated wastewater did not involve the precipitation of iron phosphate sludge, and that the substances responsible for the COD load as well as phosphates are adsorbed by colloidal micelles of iron hydroxide.

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ELEKTROKOAGULACJA ŚCIEKÓW MODELOWYCH NA ELEKTRODACH ŻELAZNYCH

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Abstrakt: W pracy przedstawiono wyniki badań laboratoryjnych procesu elektrokoagulacji ścieków modelowych na elektrodach żelaznych. Użyte ścieki okazały się podatne na oczyszczanie elektrolityczne i tym samym, jako układ modelowy, umożliwiły prowadzenie badań aż w 7 powtórzeniach, co z kolei zapewniło bazę danych nadającą się do wiarygodnej obróbki statystyczno-matematycznej. Oczyszczanie ścieków prowadzono w statycznych warunkach chronopotencjometrycznych, tj. przy stałym prądzie I = 0,3 A. Każdorazowo rejestrowano zmiany napięcia zasilania w czasie zapewniające I = const. Oznaczano zmiany pH, zawiesin i mętności, ChZT oraz fosforu ogólnego w oczyszczanych ściekach. W odróżnieniu od metody wyznaczania dawki koagulantu z równania odpowiedniej paraboli, dla badanego procesu elektrokoagulacji zaproponowano oryginalną, nową metodę obliczania dawki optymalnej elektrokoagulantu żelazowego z równania wielomianu III stopnia. Metoda ta, uzasadniona teoretycznie i praktycznie, umożliwiała każdorazowo bardzo precyzyjne określenie takiej dawki. Stwierdzono, że wzrost dawki elektrokoagulantu żelazowego w układzie prowadzi do zwiększenia udziału elektrokoagulacji „zamiatającej" w badanym procesie oczyszczania ścieków.

Słowa kluczowe: ścieki modelowe, dawka elektrokoagulantu żelazowego

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Dariusz BORUSZKO[1]

IMPACT LOW-COST PROCESSING METHODS ON THE CONTENTS OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEWAGE SLUDGE

WPŁYW NISKONAKŁADOWYCH METOD PRZETWARZANIA NA ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W OSADACH ŚCIEKOWYCH

Abstract: In Poland, more and more often to the processing of sewage sludge are used low-input methods: composting, vermicomposting, reed bed, willow energy and solar driers. Also in the north-eastern part of Poland for many years successfully operate objects using these methods.

The paper presents the experience of the use of low-cost methods of sludge treatment in wastewater treatment plant located in Zambrow, Podlaskie Province. The results of studies of sewage sludge on the PAHs content after treatment in reed bed system were presented.

In 2012, samples of sediment were taken from the middle part of the oldest red bed (still in service) in the 3-meter profile of the sediment fill. Sampling was performed using a special probe to enable the extraction of sewage sludge from the full depth of the lagoon. Samples were averaged and sediment samples from each 0.5 m section were tested.

The obtained results for the PAHs in sediments from the lagoon of sludge from reed sewage treatment plant in Zambrow show that the average content of PAHs studied is approximately 5552.8 $\mu g \cdot kg^{-1}$ d.m. At the same time, there are clear differences in the content of these compounds in each of the processed layers of sludge in the lagoon. An average contents of PAHs tested in individual layers of the sludge were as follows: 5852.2 μg PAHs $\cdot$ kg^{-1} d.m. in the upper sludge layer (0–1 m), 6636.8 μg PAHs $\cdot$ kg^{-1} d.m. in the middle sludge layer (1–2 m) and 4169.5 μg PAHs $\cdot$ kg^{-1} d.m. in the oldest, bottom sludge layer (2–3 m). A significant decrease in the total PAHs content with increasing the time period of the processing of sludge lagoons at the lowest bottom layer was observed after 10–12 years. Sewage sludge processed by California earthworms for vermicompost was characterized by the lowest total content of studied PAHs, which amounted 2550.2 $\mu g \cdot kg^{-1}$ d.m.

Keywords: polycyclic aromatic hydrocarbons, reed bed systems, sewage sludge

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Introduction

In Poland, more and more often for processing of sewage sludge low-input methods are used, *ie*: composting, vermicomposting, reed bed, willow energy and solar driers. Also in the north-eastern Poland for many years facilities are operated, in which these methods are successfully used. This sector of wastewater treatment is affected by the following factors:

- majority of waste treatment plants are small and medium-sized facilities,
- agricultural and industrial character of the region,
- character of generated sewage sludge,
- available on these areas biomass as straw, sawdust and chips,
- low quality class of the soil [1].

All these factors justify the possibility of using low-input processes on these areas.

Low-input methods of processing sewage sludge are characteristic first of all by their simple design and technology and by their easy operation. These methods allow using only a limited number of process equipment due to which the consumption of electrical energy is low. Utilisation of natural processes occurring in the environment allows maintaining low operation costs [2].

This paper presents selected examples of experience and the study of one of the first wastewater treatment plants in the Podlaskie Province in Zambrow run by the Zambrowskie Ciepłownictwo i Wodociągi sp. z o.o. (District Heating and Waterworks Zambrow Ltd), which for a dozen or so years successfully treats sewage sludge by low-cost methods [3]. The goal of the study was first of all to verify if using reed bed lagoons and vermicomposting for the PAHs decomposition process is efficient.

From the ecological point of view more important is the PAHs collection and transformation within individual ecosystems. Since nearly 90 % of the PAHs contained there come from the soil specific actions and means should be implemented to protect these ecosystems. Moreover studies so far demonstrate differences in the degree and the speed of the PAHs transformation in the soil, what proves their long life and the possibility of bioaccumulation in this environment. The PAHs (and other organic compounds) occur also in plants, thus being a great concern, as the mechanism of absorbing the PAHs and other organic compounds is not fully understood. It is assumed that it is possible due to accumulation of harmful substances on the surface of leaves during atmospheric precipitations or due to contamination with soil particles. Irrespective of that in many countries studies are conducted in order to determine the limit values for organic substance content both in sewage sludge and in composts and in potable water. In Germany there are no binding regulations concerning the PAHs content in sludge, however, a designation of 9 PAHs is recommended; the sum of which should not exceed 6000 $\mu g \cdot kg^{-1}$ d.m. In the proposed amendment to the Sediment Directive the sum of 11 hydrocarbons should not exceed 6000 $\mu g \cdot kg^{-1}$ d.m.

The Polish legislation does not provide any regulations on the maximum PAHs content in sewage sludge designed for use in the agriculture as well as there is no uniform procedure of analytic analysis of PAHs in sludge. Determination of micro-contaminations in the sewage sludge is one of the most complicated analytical tasks connected with the heterogeneity of these materials and with differentiated PAH concentrations [4].

PAHs are also in the air as vapor and aerosols defaulting on dust particles [5]. Although the PAHs content in sediments used in agriculture in Poland is not subject to norms these substances are taken into account in the draft of alterations / amendments to the UE Directive 75/442/EWG according to which a permissible summary concentration of 11 aromatic compounds (acenaphtene, phenanthrene, fluorene, fluorantene, pyrene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene) should be 6 mg · kg^{-1} (converted to dry mass) [6].

Material and methods

Sludge management in a wastewater treatment plant

In the municipal wastewater treatment plant of the Zambrow city some 1 ton d.m. of raw sewage sludge is generated per full day. The sludge management is based on sludge lagoons, reed beds and earthworm fields. Outside of the winter season 70 % of the sludge is carried away directly to a reed bed of an area 3 times 3500 m^2. In winter the sludge is directed onto sludge lagoons provided with a vertical drainage ensuring a high efficiency of the sludge dewatering when filling the lagoon. In the wastewater treatment plant there are 2 sludge lagoons of a 2500 m^3 capacity each. Approximately 80–90 % of the sludge collected on sludge lagoons is pumped in summer time onto earthworm fields of an area of some 1 ha. The remaining sludge is utilised in the agriculture, for reclamation in autumn (after harvest). This solution allows shortening the time of the sludge removal from the wastewater treatment plant down to two weeks, *ie* during emptying the sludge lagoon and after removing the sludge from earthworm fields during a period when this product is needed. Figure 1 illustrates the schematic of sludge in wastewater treatment plants in Zambrow.

In 2013 the sludge from the oldest reed lagoon will be removed after 14 years of operation.

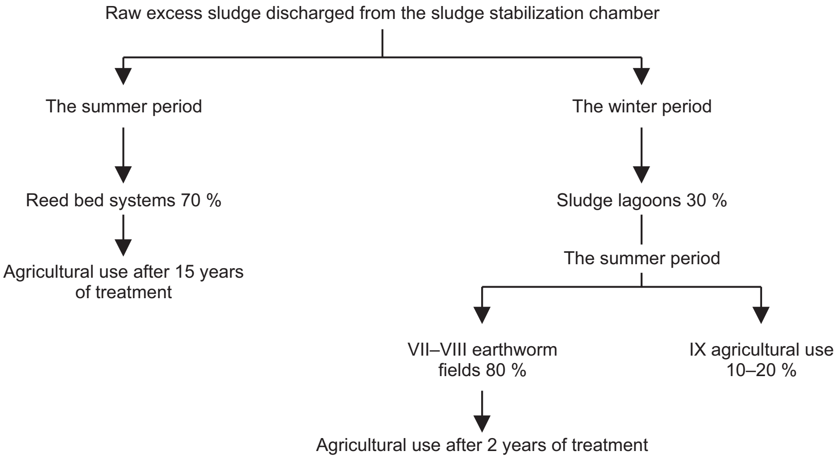

Fig. 1. Schematic of sludge in wastewater treatment plants in Zambrow

In 2013 sludge samples were taken from the middle oldest part of the operated lagoon in its 3 meter deep profile filled with the sediment. For every 0.5 m long section sludge samples were averaged and subjected to physio-chemical examination.

The method of designation of the content of selected PAHs in the biomaterial (sewage sludge) includes the way of determination of selected PAHs (Table 1) in a biomaterial of a concentration higher than 1.0 ng · g^{-1} of dry mass (of every single compound) by a high performance liquid chromatography (HPLC) with the fluorescence detection after the ultrasound extraction.

Table 1

Polycyclic aromatic hydrocarbons identified by this procedure

No.	Name of substance	Chemical formula	Molecular weight [g · mol^{-1}]	Carbon participation [%]
1	fluoranthene	$C_{16}H_{10}$	202.26	95.0
2	benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	95.2
3	benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	95.2
4	benzo(a)pyrene	$C_{20}H_{12}$	252.32	95.2
5	dibenzo(a, h)anthracene	$C_{22}H_{14}$	278.35	94.7
6	benzo(g, h, i)perylene	$C_{22}H_{12}$	276.34	95.6
7	indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	95.6

The method consisted in separation of PAHs from a biological matrix by an ultrasound method using an appropriate organic solvent (benzene) and in designation of tested compounds by the high performance liquid chromatography (HPLC). The extract was concentrated by evaporation in a nitrogen jet and the remnant was dissolved in an organic solvent (acetonitryle). Next, the PAHs mixture was separated in a chromatography column by way of the gradient elution. The identification and quantitative designation was performed by the florescence detection with programming of the wave of excitation and emission.

The identification of individual PAHs was carried out comparing the retention times of the sample peaks to the peak retention times from reference solutions by the method of a reference curve with addition of an examined matrix.

It is a different methodology than that used for the determination of PAHs in marine waters [7].

Results and discussion

The Table 2 presents averaged results of the PAHs study. The content of the following PAHs were determined in the sewage sludge: naphtalene, antracene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. Designations used in the Table 2: I – depth 0.0–0.5 m, II – depth 0.5–1.0 m, III – depth 1.0–1.5 m, IV – depth 1.5–2.0 m, V – depth 2.0–2.5 m, VI – depth 2.5–3.0 m, W – vermicompost.

Table 2

The results of dewatered sludge in the lagoon cane and vermicompost processed by California earthworms for the content of PAHs

No. PAH [µg · kg^{-1} d.m.]	I	II	III	IV	V	VI	W
Naphthalene	277.1	276.6	266.3	266.1	265.5	265.5	35.1
Anthracene	203	199	132	98.6	79.6	83.4	32.4
Fluoranthene	1630	1542	1496	1454	912	821	163.6
Benzo(b)fluoranthene	823	708	812	889	312	407	543.2
Benzo(k)fluoranthene	566	502	538	579	434	334	432.1
Benzo(a)pyrene	723	718	823	848	654	474	732.2
Dibenzo(a, h)anthracene	42.3	37.3	53	60.7	29	26	34.2
Benzo(g, h, i)perylene	865	892	1213	1319	934	864	176.1
Indeno(1,2,3-cd)pyrene	876	824	1127	1299	827	617	401.3
Total PAHs	6005.4	5698.9	6460.3	6813.4	4447.1	3891.9	2550.2

Source: Research and development of their own.

The (Fig. 2 and 3) illustrate the changes in the concentration of individual PAHs and their total deposits in the studied samples as a function of the processing time in the lagoon cane.

9 PAHs were found out in all examined samples. Referring the test results to the above-mentioned Directive excessive values were found out in three samples of the

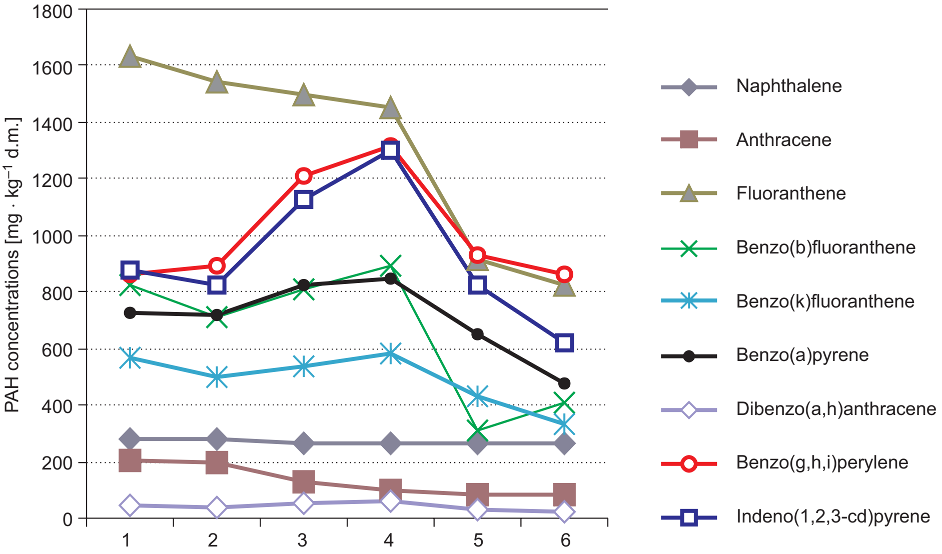

Fig. 2. Changes in concentration of individual PAHs studied depending on the processing time of sludge in the lagoon cane. Source: own research

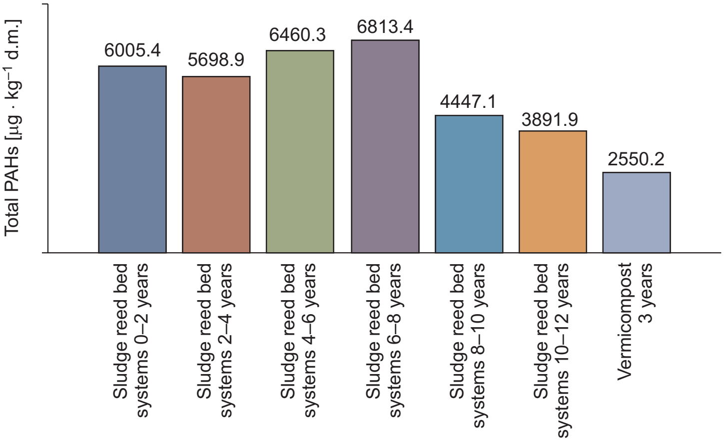

Fig. 3. Total studied PAHs content in sewage sludge, depending on the time of its lagoon cane processing. Source: own research

sediment from the reef lagoon. For sediments from a 2, 6 and 8-year time of transformation the total of the examined PAHs exceeded 6 mg · kg^{-1} d.m. In samples of the lowest sediment lagoon layers from the 10–12-year period of operation the lower concentration of the tested PAHs were found out; correspondingly at 4.4471 mg · kg^{-1} d.m. for sediments transformed for 10 years and at 3.8919 mg · kg^{-1} d.m. for sediments transformed for 12 years. The lowest sum of tested PAHs was obtained for the 3–7-year vermiculture – 2.5502 mg · kg^{-1} converted to dry mass.

Among the 9 examined PAHs of the lowest concentration was the dibenzo(a,h)anthracene, the concentration of which in not a single sample exceeded 100 µg · kg^{-1} d.m. The highest concentration was determined in case of fluoranthene and benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene; the concentration of these compounds exceeded 1000 µg · kg^{-1} d.m. (Fig. 1).

Wlodarczyk-Makula [8] has studied for the PAHs content in the soil from the Czestochowa region as well as in the sewage sludge. The sum of 16 PAHs is much lower than in sewage sludge from Zambrow as it does not exceed 1.912 µg · g^{-1} d.m., from which 60 % in three examined samples were found naphtalene and acenaphtylene. On the other hand the Zambrow sewage sludge are characterised by their low content of naphtalene, below 7 % of the PAHs sum. Bodzek [9] obtained similar results examining sewage sludge in Gorny Slask (Upper Silesia) since the sum of tested two-ring hydrocarbons, *ie* the naphtalene and dimethyl-o-phenyl did not exceed 0.3 µg · kg^{-1} d.m.

The benzo(b)fluoranthene was found in the majority of sludge samples and its highest concentration was determined in the reed lagoon after 8 years of transformation at the level of 889 µg · kg^{-1} d.m. and in the 3-year old vermicompost at the level of 543.2 µg · kg^{-1} d.m., which was 13 % to 21 % of the 9 PAHs sum. Perez [10] obtained approximate levels examining sewage sludge in Spain for the PAHs content. Measurements were carried out with the gas chromatograph and showed a relatively high concentration of benzo(b)fluoranthene – 746 μg · kg^{-1} d.m., thus constituting 26 % of the 16 PAHs sum.

The concentration of the naphtalene in case of sludge from the reef field ranged from 265.5 to 277.1 μg · kg^{-1} d.m. Results obtained by Oleszczuk [11], who examined the PAHs concentration in sludge from the reed field at a dose of 600 ton of the sewage sludge per 1 hectare, are somewhat different. He obtained the naphthalene concentration within 0.0054 to 0.0089 μg · kg^{-1} d.m.

The benzo(g,h,i)perylene concentration in samples from the reed bed lagoon ranged from 864.1 to 1319.1 μg · kg^{-1} d.m. but in case of a 3-year vermicompost was found the lowest value – 176.1 μg · kg^{-1} d.m. The PAHs concentration drop with time of composting is confirmed also by the study of Oleszczuk [12] on the example of the same hydrocarbon studied in Krasnik, where the initial value was 719.9 μg · kg^{-1} d.m., and already after 76 days only 267.8 μg · kg^{-1} d.m.

The results of the study demonstrate a high efficiency of low-cost methods used in the wastewater treatment plant in Zambrow in terms of the quality of processed sludge. Sewage sludge from the lowest layer of the reed lagoon (12–13-year of dewatering and transformation) are characterized by the lowest PAHs content. The higher a sediment layer lies, *ie* the shorter the time of processing, the higher is the PAHs content. This points to a great role of reed in accumulation of these compounds. Concerning the PAHs content in the produced compost its highest reduction was observed. A three-year processing of sludge by Californian earthworms allows achieving lower PAHs content as compared to a dozen or so years of sludge dewatering on a reed bed lagoon. This is also confirmed by other national and foreign experiments [13–15].

Conclusions

The wastewater treatment plant in Zambrow is the only facility in the Podlaskie Province in which exclusively natural, low-input methods of the sediment processing are used. On the example of solutions used in Zambrow one can state that for selection of methods of sewage sludge processing, especially such which promise to meet the conditions for the use in the nature or agriculture, also such factors as the process cost, the final utilization of the sewage sludge, the analysis risk and the environmental impact must be taken into account.

Conducted studies to determine the character of the sewage sludge from the wastewater treatment plant in Zambrow as well as effects achieved using the vermiculture and reed lagoons confirm that from the economic, ecological and environmental points of view these methods are justified. An important issue is the psychological factor, which will help to understand that the sewage sediment when properly transformed is not a dangerous waste but can be a competitive product.

According to the draft of alterations / amendments to the UE Directive 75/442/EWG excessive inadmissible concentration levels of the sum o 9 examined PAHs were stated in three samples of sewage sediments processed on a reed lagoon.

The lowest summary concentration of 9 PAHs was stated in a sewage sediment from the installation with a 3-year vermiculture, which means that vermicomposting can contribute to the reduction of the PAH concentration.

The study results indicate that the greater the number of rings in a given hydrocarbon the more difficult is the process of its mineralisation.

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WPŁYW NISKONAKŁADOWYCH METOD PRZETWARZANIA NA ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W OSADACH ŚCIEKOWYCH

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Abstrakt: W artykule przedstawiono wyniki doświadczeń z zastosowaniem niskonakładowych metod przetwarzania osadów w oczyszczalni ścieków położonej w Zambrowie, województwo podlaskie. Zostały przedstawione wyniki badań osadów ściekowych na zawartość WWA po przetworzeniu w lagunach trzcinowych oraz wermikulturę.

Uzyskane wyniki zawartości WWA w osadach z laguny trzcinowej z oczyszczalni ścieków w Zambrowie pokazują, że średnia zawartość WWA wynosiła 5552,8 μg · kg^{-1} sm. Jednocześnie istnieją wyraźne różnice w zawartości tych związków w każdej z przebadanych warstw osadu w lagunie. Górna warstwa osadu (0–1 m) zawiera średnio 5852,2 μg · kg^{-1} s.m. badanych WWA, środkowa warstwa osadu (1–2 m) zawiera średnio 6636,8 μg · kg^{-1} s.m., a najstarsza dolna warstwa osadów (2–3 m) wskazuje średnio najmniejszą zawartość 4169,5 μg · kg^{-1} s.m. WWA. Zaobserwowano wyraźne zmniejszenie zawartości sumy WWA wraz z wydłużaniem okresu czasu przetwarzania na lagunach w najniższej dolnej warstwie osadu stwierdzoną po 10–12 latach. Osad ściekowy przetworzony przez dżdżownice kalifornijskie na wermikompost charakteryzował się najmniejszą zawartością sumy badanych WWA, wynoszącą 2550,2 μg · kg^{-1} s.m.

Słowa kluczowe: WWA, laguna trzcinowa, osady ściekowe

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SEASONAL CHANGES OF SELENIUM AND SELECTED OXIDOREDUCTASES IN SOIL UNDER MANURE AND NITROGEN FERTILZATION

SEZONOWE ZMIANY ZAWARTOŚCI SELENU ORAZ AKTYWNOŚCI WYBRANYCH OKSYDOREDUKTAZ W GLEBIE W WARUNKACH NAWOŻENIA OBORNIKIEM I AZOTEM

Abstract: The aim of the study was to determine the changes of total and available Se concentrations in soil and some oxidoreductases activity in relation to applied doses of fertilizers over vegetation period. The experiment was conducted applying the following crop rotation system – potato – winter wheat with intercrop – spring barley+ undersown – red clover and grasses designed in a split-plot with four replications. The soil was fertilized with farmyard manure (FYM) at doses 0, 20, 40, 60 and 80 Mg $\cdot$ ha^{-1} (under potato) and with nitrogen at rates 0, 30 and 60 kgN $\cdot$ ha^{-1} under red clover and grasses. Total selenium content in soil under red clover and grasses cultivation ranged from 132 to 169 μg $\cdot$ kg^{-1}, what indicates that analysed soil is poor in this microelement. FYM fertilization significantly increased total selenium content in the soil with increasing doses of this fertilizer. The highest amounts of total selenium were found in soil at the beginning of the investigation period. The highest content of phytoavailable fractions and their share in the total selenium were observed in the case of fertilization with FYM at a dose of 40 Mg $\cdot$ ha^{-1} and then decreased with increasing doses of FYM. FYM fertilization as well as mineral nitrogen stimulated the activity of the investigated oxidoreductases, in comparison with non fertilized soil. The highest amounts of enzymes activity were obtained in July. The calculated correlation coefficients between total selenium and organic carbon and total nitrogen content in soil; enzymes activity and organic carbon and total nitrogen and between total selenium content and DHA activity, confirmed a close inter-relationship among these parameters.

Keywords: selenium, available fractions, dehydrogenases, catalase, farmyard manure, nitrogen

Introduction

Selenium is an essential nutrient for animals, microorganisms and some other eukaryotes. Although selenium has not been demonstrated to be essential in vascular

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plants, the ability of some plants to accumulate and transform selenium into bioactive compounds has important implications for human nutrition and health, and for the environment [1]. Selenium exists in four valence states, of which the 2-state predominates in organic Se compounds. Commonly occurring species, selenites (Se^{4+}) and selenates (Se^{6+}), do not form stable compounds in geochemical environments and are preferably adsorbed by minerals, particularly clay minerals, and Fe and Mn oxides as well as hydroxides [2].

Selenium is primarily taken up from the soil by plants as selenate or selenite. Selenate directly competes with sulfate for uptake by plants [1]. The factors which control Se mobility and availability in soils are pH, redox conditions and soil organic matter (SOM) content [2]. Redox conditions and pH determine the Se species in a soil environment, but in most conditions selenate and selenite are the main species. Selenate is predominant at near-neutral reaction and under aerobic conditions, whereas selenite is the main species at acid reaction and lower redox potential. Selenite is tightly bound to clay particles and Fe/Al oxides and thus only little available for plant uptake. Selenate is only weakly sorbed by soil particles, more mobile in the soil solution and therefore more plant-available [3].

According to Samuel et al [4], dehydrogenase activity of a soil is an indicator of biological redox-systems and can be considered as a measure of the intensity of microbial metabolism in soil. The catalase of aerobic organism splits the toxic H_2O_2 produced from the mitochondrial electron transport and from various hydroxylation and oxygenation reactions into water and oxygen [4]. Since aerobic organism predominates in non-compacted and non-waterlogged soils, catalase activity was used to characterize soil microbial activities.

The objective of this study was to evaluate the effects of organic and mineral fertilization on the available to plants forms of selenium and dynamics of dehydrogenases and catalase activity affecting the selenium status in soil.

Materials and methods

Soil samples were collected from the long-term static experiment established at the Agricultural Experimental Station at Grabow carried out since 1980 by the Department of Plant Nutrition of the Institute of Soil Science and Cultivation in Pulley (Poland). The experiment was conducted applying crop rotation “enriching in organic matter” (potato – winter wheat + intercrop – spring barley + undersown and red clover + grasses), designed in a split-plot with four replications (sub-plots). Organic fertilizer in a form of cattle manure (FYM) was applied under potato at the doses of 0, 20, 40, 60 and 80 $Mg \cdot ha^{-1}$ (factor I) and nitrogen in a form of ammonium nitrate at 0, 30 and 90 $kgN \cdot ha^{-1}$ under red clover and grasses (factor II). Soil samples were collected in March, May and July (factor III) 2004, from the 0–20 cm layer under red clover (‘Jubilatka’ cv.) and grasses. Soil samples were air-dried and sieved through a 2 mm screen.

Soil samples were analysed for granulometric composition according to Bouyoucoss-Cassagrande method, organic carbon (TOC) by wet oxidation with potassium dichromate, total nitrogen (TN) following by Kjeldahl method and pH potentiometrically in distilled water and 1 mol · dm^{-3} KCl solution [5].

Total selenium content in soils was determined by the method of Watkinson [6] using a Hitachi F-2000 spectrofluorometer. Samples were microwave digested with concentrated nitric and perchloric acids. The different forms of selenium in the samples were reduced by boiling with 10 % HCl. The selenium was complexed with 2,3-diaminonaphtalene (DAN) to give the fluorescent compound, which was extracted with cyclohexane and read on a spectrofluorometer at excitation and emission wave lengths of 376 and 519 nm, respectively. The analytical procedures gave satisfactory values for the standard reference material CRM024-050 Resource Technology Corporation (RTC), soil from Western US of a texture of loamy sand; 0.558 mgSe · kg^{-1} (certified value 0.540 mgSe · kg^{-1}). Available to plants forms of selenium were extracted from the soil by the part of sequential extraction method recommended by Chao and Sanzolone [7] with modification of Wang and Chen [8]. Firstly, 0.25 mol · dm^{-3} KCl solution was used to extract the soluble form of selenium (Se^{6+}). The exchangeable and specifically adsorptive forms of selenium (Se^{4+}) were extracted by 0.1 mol · dm^{-3} KH_2PO_4 solution. The final reaction solution of each extraction was adjusted with dilute HCl to a pH range 1.7–2.0. The selenite (Se^{4+}) was then chelated by adding 2,3-diaminonaphtalene to the solution and determined by fluorescence spectrophotometry [6].

Dehydrogenases activity (DHA) were assayed applying the method by Casida et al [9]. Soil DHA activity was estimated by reducing 2,3,5-triphenyltetrazolium chloride. Soil sample was mixed with $CaCO_3$ and 2,3,5-triphenyltetrazolium chloride (TTC) and incubated for 24 h at 37 °C. Dehydrogenase converts TTC to 2,3,5-triphenylformazan (TPF). The TPF formed was extracted with acetone, the extracts were filtered and absorption was measured at 485 nm spectrophotometrically. The enzyme activities were expressed as mg triphenyltetrazolium formazan (TPF) · g^{-1} · 24 h^{-1}.

Catalase activity (CAT) was measured using the method by Johnson and Temple [10]. Soil was incubated with hydrogen peroxide for 20 min at 20 °C. The remaining H_2O_2, not broken-down by catalase, was treated with potassium permanganate exposed to H_2SO_4. To eliminate a probable overestimation of enzyme activity due to chemical reduction of H_2O_2 added, a correction for autoclaved soil (0.1 MPa, 120 °C, 30 min) was made. The results were expressed in mg H_2O_2 consumed · g^{-1} · min^{-1}.

Three-way and two-way analysis of variance (ANOVA) was used to identify significant differences ($p < 0.05$) between TOC, TN, Se concentrations and enzymes activity in studied soils. Data analysis was carried out using Statistica 8.0 for Windows Stat.Soft. Inc.

Results and discussion

The soil, according to the FAO classification, was classified as Haplic Luvisols and demonstrated the texture of loamy sand and sandy loam. pH values measured in KCl and H_2O were in the ranges: 5.4–5.6 and 6.1–6.3, respectively (Table 1).

Table 1

General properties of the investigated soil

FYM dose [t · ha^{-1}]	N dose [kg · ha^{-1}]	Share of soil particles fraction		pH	
		< 0.02 mm	< 0.002 mm	in H_2O	in KCl
		[%]			
0	N0	18	6	6.1	5.5
	N1	17	6	6.3	5.5
	N2	19	8	6.3	5.4
20	N0	14	5	6.2	5.5
	N1	16	8	6.1	5.4
	N2	15	6	6.1	5.4
40	N0	19	8	6.2	5.5
	N1	17	6	6.2	5.4
	N2	13	5	6.2	5.4
60	N0	16	5	6.2	5.5
	N1	16	6	6.2	5.4
	N2	19	7	6.2	5.6
80	N0	15	4	6.2	5.5
	N1	16	6	6.3	5.6
	N2	15	5	6.3	5.4

The content of organic carbon (TOC) in the studied soil varied from 7.55 to 10.05 g · kg^{-1}, depending upon FYM doses and nitrogen fertilization (Table 2). The highest increase in TOC was observed for treatments with 60 and 80 Mg · ha^{-1} of FYM. Soil samples from the treatment without FYM contain 24 % less TOC than those from the treatment with the highest dose of FYM. Nitrogen fertilization affected TOC and TN. The content of organic carbon in the soil was the highest after applying the highest dose of nitrogen.

Table 2

Total organic carbon and total nitrogen content in the investigated soil

FYM dose [Mg · ha^{-1}] (Factor A)	N dose [kg · ha^{-1}] (Factor B)	TOC	TN
		[g · kg^{-1}]	
0	N0	7.55	0.679
	N1	7.60	0.683
	N2	7.14	0.711
20	N0	8.10	0.707
	N1	7.89	0.721
	N2	8.05	0.739

Table 2 contd.

FYM dose [Mg · ha^{-1}] (Factor A)	N dose [kg · ha^{-1}] (Factor B)	TOC	TN
		[g · kg^{-1}]	
40	N0	8.37	0.749
	N1	7.61	0.728
	N2	9.24	0.812
60	N0	9.67	0.854
	N1	9.87	0.826
	N2	10.05	0.861
80	N0	9.35	0.917
	N1	9.94	0.931
	N2	9.78	0.959
Mean for FYM doses (Factor A)	0	7.43	0.664
	20	8.01	0.725
	40	8.41	0.748
	60	9.66	0.814
	80	9.79	0.859
Mean for N doses (Factor B)	N0	7.81	0.739
	N1	7.78	0.750
	N2	8.05	0.771
$LSD_{0.05}$		A – 0.022; B – 0.018	A – 0.002; B – 0.001

Total selenium content in the soil samples ranged from 110 to 249 μg · kg^{-1} (Table 3).

We observed the increase of total selenium content almost 28 % in soil fertilized with the highest dose of FYM in comparison with soil from control plots. This may have been consequence by the amount of this microelement in farmyard manure, which was at the rate of 2.24 mg · kg^{-1}. Such low levels of selenium in soils indicated that plants growing on these soils are deficient in this microelement. According to Kabata-Pendias [2], the mean total selenium content in the soils worldwide is estimated as 0.44 mg · kg^{-1}, while its background contents in various soil groups range from 0.05 to 1.5 mg · kg^{-1}. The selenates and selenites content in the soil samples fluctuating between 16–35 μg · kg^{-1} and 15–43 μg · kg^{-1}, respectively (Table 3).

An increase in selenates and selenites was observed after application of FYM in comparison with control plots, but the highest contents of both of these ions were recorded in soil samples collected from plots fertilized with 40 Mg · ha^{-1} of FYM. The opposite tendency was noted in the case of a plot fertilized with the highest doses of FYM. The use of nitrogen fertilizer at 30 kgN · ha^{-1} caused an increase in selenates concentration in the studied soil. During vegetation period of red clover and grasses the total content of selenium and its phytoavailable fractions in the soil decreased.

Kabata-Pendias [2] was of the opinion that low mobility of selenium occurs in soils with high contents of hydroxides, clay granulometric fractions and soil organic matter, which may act the reduction of selenate to selenite and thus reduce Se availability in soils.

Table 3

Total and phytoavailable fractions content of selenium in the studied soil under red clover [μg · kg^{-1}]

FYM dose [Mg · ha^{-1}] (Factor A)	N dose [kg · ha^{-1}] (Factor B)	Total Se			SeF1 (Se VI)			SeF2 (Se IV)		
		Date of sampling (Factor C)								
		March	May	July	March	May	July	March	May	July
0	N0	132	150	110	19	22	21	29	27	23
	N1	128	150	125	20	18	23	25	23	25
	N2	131	141	117	20	23	22	22	23	20
20	N0	165	132	144	18	16	13	19	17	16
	N1	121	142	135	21	23	26	21	23	24
	N2	145	132	140	23	25	23	22	24	20
40	N0	156	160	128	26	27	29	43	40	38
	N1	169	124	184	32	34	36	30	32	35
	N2	160	124	132	31	30	26	29	27	26
60	N0	164	180	123	27	25	23	22	19	16
	N1	156	174	116	29	26	23	23	22	19
	N2	178	187	134	22	19	16	22	18	15
80	N0	168	124	189	23	20	16	25	22	19
	N1	168	127	249	33	29	27	35	31	27
	N2	184	184	122	25	22	19	23	19	17
Mean for FYM doses (Factor A)										
	0	132			21			24		
	20	139			21			21		
	40	149			30			33		
	60	158			23			19		
	80	169			24			24		
Mean for N doses (Factor B)										
	0	149			22			25		
	N1	152			26			26		
	N2	148			23			22		
Mean for date of sampling (Factor C)										
	March	155			24			26		
	May	149			24			24		
	July	143			23			23		
	$LSD_{0.05}$	A – 3.11; B – 1.08; C – 1.23			A – 1.13; B – 1.21; C – 1.34			A – 1.14; B – 1.22; C – 1.28		

The activity of DHA over the vegetation period in the analysed soil fluctuated between 0.018 and 0.058 mg TPF · g^{-1} · 24 h^{-1} (Table 4). Fertilization with FYM and nitrogen significantly stimulated the activity of this enzyme, along with increasing doses of both fertilizers.

Table 4

Enzymatic activity in soil under study

FYM dose [Mg · ha^{-1}] (Factor A)	N dose [kg · ha^{-1}] (Factor B)	DHA activity [mg TPF · g^{-1} · 24h^{-1}]			CAT activity [mg H_2O_2 · g^{-1} · min^{-1}]		
		Date of sampling (Factor C)					
		March	May	July	March	May	July
0	0	0.019	0.030	0.032	0.040	0.051	0.085
	N1	0.017	0.030	0.035	0.051	0.053	0.102
	N2	0.018	0028	0.030	0.053	0.047	0.102
20	0	0.023	0.040	0.030	0.051	0.060	0.102
	N1	0.025	0.033	0.037	0.047	0.055	0.104
	N2	0.031	0.035	0.032	0.060	0.055	0.109
40	0	0.032	0.034	0.033	0.053	0.057	0.109
	N1	0.029	0.036	0.039	0.055	0.060	0.115
	N2	0.032	0.038	0.046	0.045	0.057	0.113
60	0	0.032	0.046	0.050	0.045	0.057	0.119
	N1	0.030	0.044	0.054	0.051	0.066	0.113
	N2	0.036	0.048	0.056	0.047	0.060	0.113
80	0	0.041	0.047	0.057	0.047	0.060	0.119
	N1	0.043	0.046	0.056	0.051	0.057	0.115
	N2	0.038	0.042	0.058	0.053	0.055	0.115
Mean for FYM doses (Factor A)							
	0	0.027			0.064		
	20	0.032			0.071		
	40	0.036			0.075		
	60	0.044			0.075		
	80	0.048			0.075		
Mean for N doses (Factor B)							
	0	0.037			0.071		
	N1	0.037			0.073		
	N2	0.038			0.072		
Mean for date of sampling (Factor C)							
	March	0.030			0.050		
	May	0.038			0.057		
	July	0.044			0.109		
	$LSD_{0.05}$	A – 0.002; B – 0.001; C – 0.003			A – 0.004; B – 0.001; C – 0.002		

Manure application differentiated CAT activity in soil (Table 4). During vegetation period manure fertilization strongly stimulated soil catalase activity with increasing doses, especially after application of 80 $Mg \cdot ha^{-1}$, in comparison with the control soil. The highest CAT activity was recorded after applying ammonium nitrate with the dose of 30 $kg\ N \cdot ha^{-1}$, in comparison with a soil from plot not fertilized with nitrogen.

Enzymatic activity in studied soil demonstrated clear seasonal variations and considerable fluctuations depending on climatic conditions and availability of substrate. The highest amounts of DHA as well as CAT activities were observed in soil collected in July. Mocek-Plociniak [11] stated that adequately high moisture of soil is a fundamental condition of soil enzymes activity.

Significant correlations were found for the relationship between the total selenium content and organic carbon and total nitrogen. Positive Pearson indexes were also found for: dehydrogenases activity and organic carbon and total nitrogen; catalase activity and organic carbon and total nitrogen (Table 5). At the beginning of vegetation period (in soil samples collected in March) we found close inter-relationship between total selenium content and DHA activity ($r = 0.77$).

Table 5

Simple correlation coefficients (r) between selenium content and enzymatic activity and soil properties

Examined properties	Fraction < 0.002	pH_{H_2O}	pH_{KCl}	TOC	NT	Se_{tot}	Se VI	Se IV	DHA	CAT
Fraction < 0.02	0.62*	–0.21*	–0.23*	0.29*	0.30*	0.25*	0.03	0.07	0.22*	0.21*
Fraction < 0.002		0.00	0.12	0.39*	0.40*	0.25*	0.12	0.24	0.22*	0.30*
pH_{H_2O}			–0.03	–0.04	–0.07	–0.11	–0.12	–0.15	–0.04	0.05
pH_{KCl}				0.22*	0.21*	0.18	0.14	0.17	0.11	0.20*
TOC					0.88*	0.40*	0.38	0.33	0.92*	0.71*
NT						0.44*	0.37	0.31	0.94*	0.78*
Se_{tot}							0.21	0.15	0.31	0.35

* r significant at $\alpha = 0.05$.

Many authors [4, 12–14] reported that increase inputs of organic residue, plant or animal manures, increase biological activity. FYM treatment usually increases microbial biomass and soil enzyme activities compared to soils without any organic or inorganic amendments. Thus management practices that increase incorporation of organic residue typically increase biological activity. Use of inorganic fertilizer can increase the plant biomass production which in turn increases the amount of residue returned to the soil and stimulates biological activity.

Conclusions

Total selenium content in soil under red clover cultivation ranged from 110 to 249 $\mu g \cdot kg^{-1}$, what indicate that the analysed soil is poor in this microelement. FYM

fertilization significantly increased total selenium content in the soil with increasing doses of this fertilizer. The application of the highest dose of FYM caused an increase of total selenium about 28 % compared with control. The highest amounts of total selenium were found in soil at the beginning of the investigation period. The highest content of phytoavailable fractions were observed in the case of fertilization with FYM at a dose of 40 Mg · ha^{-1} and then decreased with increasing FYM doses. FYM fertilization and applied nitrogen stimulated the activity of the investigated oxidoreductases, in comparison with control. The highest enzymes activity was observed in July. We found close inter-relationship between total selenium content and organic carbon and total nitrogen content in soil; enzymes activity and organic carbon and total nitrogen and between total selenium content and DHA activity.

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SEZONOWE ZMIANY ZAWARTOŚCI SELENU ORAZ AKTYWNOŚCI WYBRANYCH OKSYDOREDUKTAZ W GLEBIE W WARUNKACH NAWOŻENIA OBORNIKIEM I AZOTEM

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Abstrakt: Celem pracy było określenie zmian zawartości selenu przyswajalnego dla roślin oraz aktywności wybranych enzymów uczestniczących w przemianach oksydoredukcyjnych w glebie w warunkach zróżnicowanego nawożenia. Próbki gleby pochodziły z doświadczenia prowadzonego przez IUNG w Puławach na terenie RZD Grabów nad Wisłą, z wariantu wzbogacającego glebę w substancję organiczną, z następującym doborem roślin w zmianowaniu: ziemniaki – pszenica ozima + międzyplon – jęczmień jary z wsiewką – koniczyna z trawami. Próbki pobrano czterokrotnie (w marcu, maju, lipcu i wrześniu) w 2001 r. z obiektów, na których uprawiano koniczynę czerwoną. Nawożenie obornikiem zastosowano (jednorazowo w trakcie rotacji) pod ziemniaki w dawkach 0, 20, 40, 60 i 80 Mg · ha^{-1}, natomiast pod koniczynę czerwoną z trawami zastosowano azot w postaci saletry amonowej w ilości 0, 40 i 120 kgN · ha^{-1}. Fitoprzyswajalne formy selenu wyekstrahowano z gleby, wykorzystując część analizy specjacyjnej zgodnie z metodą Chao i Sanzolone (1989) w modyfikacji Wang i Chen (2003), a następnie oznaczono metodą Watkinsona (1966) przy użyciu spektrofluorymetru F-2000 firmy Hitachi. Aktywność dehydrogenaz (DHA) oznaczono metodą Casida (1964), a katalazy (CAT) metodą Johnsona i Temple (1964). Ogólna zawartość selenu w glebie pod koniczynę czerwoną z trawami wahała się od 132 do 169 μg · kg^{-1}, co oznacza glebę ubogą w ten mikroelement. Wykazano, że nawożenie obornikiem w glebie pod uprawą koniczyny czerwonej z trawami wpływało istotnie na zawartość selenu przyswajalnego dla roślin. Niezależnie od terminu pobierania próbek glebowych, zastosowanie największej dawki obornika spowodowało istotne zwiększenie zawartości tych frakcji selenu w glebie. Nie wykazano natomiast jednoznacznego wpływu azotu w tym zakresie. Zawartość oznaczonych fitoprzyswajalnych frakcji selenu w środowisku glebowym oraz aktywność wybranych enzymów podlegała stałym wahaniom i wykazywała zmienność sezonową. Nawożenie obornikiem wyraźnie stymulowało aktywność enzymatyczną gleby. Obliczone wartości współczynników korelacji wykazały istotne zależności między aktywnością badanych enzymów glebowych a zawartością węgla organicznego i ogólną zawartością azotu.

Słowa kluczowe: selen, frakcje przyswajalne, dehydrogenazy, katalaza, obornik, azot

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SOLUBILITY OF HEAVY METALS IN SOIL FERTILIZED WITH COMPOSTS WITH POLYMER SUPPLEMENTS

ROZPUSZCZALNOŚĆ METALI CIĘŻKICH W GLEBACH NAWOŻONYCH KOMPOSTAMI Z DODATKIEM TWORZYW POLIMEROWYCH

Abstract: Application of composts from municipal waste for fertilization, due to their high content of organic matter and nutrients, generally positively affects crop yield and soil properties. Their production is based on biodegradable fractions of municipal waste, often originating from non-selective collection and therefore they may contain some quantities of pollutants, both organic and mineral, such as heavy metals, which may negatively affect the soil fertility.

In the pot experiment was investigated the effect of composts with an admixture of polymer materials modified with starch as biocomponent, on heavy metal solubility in the tested substrata on which oats and mustard were cultivated. Composts were applied to two soils with natural heavy metal contents, as well as to the soil and post-flotation sediment from zinc and lead ores processing polluted with heavy metals. The 5 composts used for fertilization were prepared from a substrate composed of wheat and rape straw and waste from pea cleaning with an eight percent admixture of polymer foils differing with the starch proportion and density. Speciation analysis of selected heavy metals was conducted using sequential extraction method by Zeien and Brümmer.

On the basis of conducted analysis it was established that the contents of individual forms of metals to the highest degree depended on the analysed element and applied substratum, whereas a supplement of composts with 8 % admixture of various polymer foils as a rule had no significant effect on the distribution of metal contents in the analysed fractions. The biggest amounts of cadmium in soil were assessed in the exchangeably bound fraction, in manganese oxides bonds and in the residual fraction, most strongly bound to solid soil phase. In the post-floatation sediment the biggest quantities of cadmium were assessed in the residual fraction and bound to crystalline iron oxides. The highest amounts of copper were bound to organic matter and natural minerals. In comparison with mineral fertilization, application of composts with polymer supplement decreased the content of copper mobile forms. Nickel, except the post-floatation sediment, occurred in the analysed substrata mainly in hardly available forms. Much greater nickel mobility was revealed in the

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post-floatation waste, where this metal, beside the residual fraction, occurred in considerable quantities in the mobile and exchangeable fractions.

Keywords: heavy metals, sequential extraction, soil, post-floatation sediment, compost, polymer

Introduction

Due to a considerable content of organic matter and nutrients, application of composts from municipal waste as fertilizer materials generally positively affects the crop yield and soil properties. Beside soil enrichment in nutrients, organic matter supplied to the soil improves its sorption properties, increases retention capacities of light soils and loosens heavy soil structure. Their production is based on greatly diversified materials. Most frequently these are the residue of biomass processing, mixed municipal waste or biodegradable fractions of municipal waste separated from them [1]. Frequently municipal waste come from a non-selective collection and therefore may contain some amounts of pollutants, both organic and mineral, such as heavy metals which are factors posing a serious hazard to the purity of the soil environment [2]. For this reason, heavy metal contents in composts may be a factor preventing the compost use for fertilization [1, 3]. In order to reduce the risk of excessive heavy metal accumulation in the environment, The Minister of Agriculture and Rural Development issued an executive regulation implementing the law on fertilizers and fertilization [4], which specified the maximum, allowable heavy metal contents in marketed organic fertilizers, also including composts. Total heavy metal content in composts allows to determine their usefulness for agricultural purposes. However, the problem with using this kind of fertilizer materials concerns not only the amount of heavy metals supplied to the soil, but also the rate at which they become mobilized [5, 6]. Information about total metal content does not allow to estimate their mobility and bioavailability after compost application to the soil. The assessment of the directions and rate of transformations which heavy metal undergo in soil may be conducted by means of sequential analysis which allows to determine the content of individual element forms and assess the hazard for the biosphere resulting from their presence.

The aim of the research was determining the changes in heavy metal solubility after application of composts with a supplement of polymer materials modified with starch on Cd, Cu and Ni solubility in three different substrata, on which oat was cultivated and white mustard as consecutive crop.

Materials and methods

The research was conducted in 2012 on the basis of a pot experiment in a vegetation hall, using five composts on three substrata, which were light and medium soils with natural heavy metal contents and soil and post-floatation sediment from zinc and lead ore processing, polluted with heavy metals. On each substratum seven fertilizer treatments were maintained: control – without fertilization (1), mineral NPK treatment (2), and objects where composts were added (3–7) (Table 1). All objects were maintained in three replications.

Table 1

The content of selected mineral components in composts used in the experiment

Share of components in composts	N	P	K	Cd	Cr	Cu	Ni	Pb	Zn
	$[g \cdot kg^{-1}$ d.m.]			$[mg \cdot kg^{-1}$ d.m.]					
Compost 1 (C1): Biomass as a mixture of wheat straw, rape straw, pea waste 1:1:0.5	8.8	3.9	14.6	2.0	14.3	17.6	8.6	4.2	175.8
Compost 2 (C2): Biomass* + 8 % foil B37 (polyethylene C – 47.5 %, thermoplastic corn starch – 45 %, compatibilizer 7.5 %)	5.8	3.3	12.2	1.1	13.0	7.4	6.8	2.7	148.9
Compost 3 (C3): Biomass* + 8 % foil B36 (polyethylene C – 65 %, thermoplastic corn starch – 30 %, compatibilizer 5 %)	5.3	3.5	12.2	1.0	12.7	5.6	6.7	2.3	138.0
Compost 4 (C4): Biomass* + 8 % foil B22 (polyethylene C – 65 %, thermoplastic corn starch – 30 %, compatibilizer – copolymer 5 %)	7.0	2.9	9.6	0.8	10.9	5.4	5.8	2.2	117.0
Compost 5 (C5): Biomass* + 8 % foil B22 (polyethylene C – 65 %, thermoplastic corn starch – 30 %, compatibilizer – copolymer 5 %) + microbiological vaccine	8.5	3.2	10.0	0.8	11.0	5.6	6.0	2.8	118.4

* as in C1.

Light soil revealed neutral pH, medium soil slightly acid and the post-floatation sediment slightly alkaline. In comparison with the light soil, medium soil was between two to three times more abundant in organic C, N, P and K and contained only slightly bigger quantities of heavy metals. Macroelements content in the post-floatation sediment was on a very low level, reaching only from several to a dozen or so percent of their content in soils, whereas the contents of analysed heavy metals were from two (copper and nickel) to over sixty (cadmium) times higher than in soils.

The composts used for the experiment were made from a mixture of wheat and rape straw and waste from pea cleaning with an eight percent admixture of polymer foils differing with starch proportion (Table 1). Obtained composts revealed a relatively small diversification of minerals. The highest contents of heavy metals were registered in the compost to which no polymer materials were added (C1). Contents of three analysed metals in the other composts were generally on a similar level. The materials were characterized by about twice lower cadmium and copper contents, and only slightly lower content of nickel in comparison with compost 1 (Table 1). Organic fertilizers were used in doses containing 0.2 g N per 1 kg of substratum. On organic fertilizer treatments the amounts of phosphorus and potassium have been aligned to the mineral salts level allowing to maintain the optimal N : P_2O_5 : K_2O ratio (1 : 0.3 : 1.37). The amount of macroelements supplied to the object fertilized exclusively with mineral fertilizers was by half lower than on compost treatments.

Oats were sown on 14 May into pots filled with 3 kg d.m. of analysed substrata mixed with the admixtures, according to the experimental design presented in Table 1. The crop was harvested after 63 days of vegetation and then white mustard was sown and gathered after 72 days of cultivation. When the experiment was completed, the soil was sampled and subjected to speciation analysis of selected heavy metals by means of sequential extraction method according to Zeien and Brummer [7]. The element content in the extracts was assessed using atomic emission spectrometer ICP-OES. Subsequent extractions identified seven fractions of heavy metals:

– F1 – mobile – active fraction (using 1 mol · dm^{-3} NH_4NO_3),

– F2 – exchangeable – auxiliary fraction (using 1 mol · dm^{-3} NH_4OAc, pH = 6.0),

– F3 – fraction of bonds bound to MNO_{xc} (1 mol · dm^{-3} NH_2OH-HCl + NH_4OAc, pH=6.0),

– F4 – fraction of organic bonds (0.25 mol · dm^{-3} NH_4EDTA, pH = 4.6),

– F5 – fraction of amorphous bonds FeO_x (0.2 mol · dm^{-3} ammonium oxalate, pH = = 3.25),

– F6 – fraction of strongly crystalline bonds FeO_x (0.2 mol · dm^{-3} ammonium oxalate + 1 mol · dm^{-3} ascorbic acid, pH = 3.25),

– F7 – residual fraction (concentrated HNO_3 and $HClO_4$).

Statistical computations and graphic presentation of the results were prepared using Statistica w. 10 PL and Microsoft Office Excell 2003 calculation sheet. The significance of differences between means was tested on the basis of one-way ANOVA and Tukey's test, identifying homogenous groups.

Results and discussion

Irrespective of the proportion of individual components in the initial mass, the composts used in the investigations met the requirements of the Regulation of the Minister of Agriculture and Rural Development [4] in view of allowable pollution with heavy metals. Total content of cadmium ranged from 16 to 40 % of the allowable value, *ie* 5 mg $\cdot$ kg^{-1} d.m., whereas nickel constituted only from 9.7 to 14.3 % (Ni quantity cannot exceed 60 mg $\cdot$ kg^{-1} d.m.), and copper content is not limited.

Application of various fertilizer variants has a relatively slight effect on cadmium content in the individual fractions and their share in total metal content (Table 2, Fig. 1).

Table 2

Content of different cadmium forms in substrata after experiment [mg $\cdot$ kg^{-1} d.m.]

Treatment	Content							
	F1*	F2	F3	F4	F5	F6	F7	Total**
Light soil								
Control	0.08^{c***}	0.39^{a}	0.20^{b}	0.08^{b}	0.16^{a}	0.09^{b}	0.22^{a}	1.22^{b}
Mineral fertilizers	0.00^{a}	0.36^{a}	0.13^{ab}	0.00^{a}	0.17^{a}	0.00^{a}	0.18^{a}	0.84^{a}
Compost 1	0.00^{a}	0.32^{a}	0.12^{a}	0.07^{b}	0.17^{a}	0.00^{a}	0.15^{a}	0.82^{a}
Compost 2	0.00^{a}	0.38^{a}	0.10^{a}	0.00^{a}	0.15^{a}	0.00^{a}	0.18^{a}	0.82^{a}
Compost 3	0.00^{a}	0.29^{a}	0.12^{ab}	0.07^{b}	0.14^{a}	0.00^{a}	0.15^{a}	0.77^{a}
Compost 4	0.00^{a}	0.32^{a}	0.12^{ab}	0.08^{b}	0.13^{a}	0.00^{a}	0.14^{a}	0.80^{a}
Compost 5	0.05^{b}	0.29^{a}	0.15^{ab}	0.00^{a}	0.18^{a}	0.00^{a}	0.15^{a}	0.82^{a}
Medium soil								
Control	0.00^{a}	0.33^{a}	0.14^{a}	0.00^{a}	0.10^{a}	0.00^{a}	0.16^{a}	0.73^{a}
Mineral fertilizers	0.00^{a}	0.37^{ab}	0.14^{a}	0.00^{a}	0.19^{a}	0.00^{a}	0.18^{a}	0.87^{ab}
Compost 1	0.00^{a}	0.35^{ab}	0.16^{a}	0.00^{a}	0.18^{a}	0.00^{a}	0.16^{a}	0.86^{ab}
Compost 2	0.00^{a}	0.34^{a}	0.12^{a}	0.00^{a}	0.18^{a}	0.00^{a}	0.16^{a}	0.79^{ab}
Compost 3	0.00^{a}	0.46^{b}	0.14^{a}	0.00^{a}	0.17^{a}	0.00^{a}	0.18^{a}	0.94^{b}
Compost 4	0.00^{a}	0.35^{ab}	0.12^{a}	0.00^{a}	0.15^{a}	0.00^{a}	0.16^{a}	0.77^{ab}
Compost 5	0.00^{a}	0.35^{ab}	0.11^{a}	0.00^{a}	0.17^{a}	0.00^{a}	0.14^{a}	0.77^{ab}
Post-flotation sediment								
Control	7.71^{a}	13.18^{c}	2.03^{a}	1.49^{a}	0.00^{a}	1.26^{a}	33.99^{c}	59.66^{c}
Mineral fertilizers	7.06^{a}	12.84^{bc}	2.11^{a}	1.36^{a}	0.00^{a}	1.19^{a}	30.87^{c}	55.42^{bc}
Compost 1	7.58^{a}	11.87^{abc}	2.07^{a}	1.52^{a}	0.00^{a}	1.17^{a}	25.39^{b}	49.59^{a}
Compost 2	7.24^{a}	12.29^{abc}	2.08^{a}	1.57^{a}	0.00^{a}	1.24^{a}	22.61^{ab}	47.02^{a}
Compost 3	7.21^{a}	12.75^{a}	2.33^{a}	1.63^{a}	0.00^{a}	1.23^{a}	21.05^{ab}	46.20^{a}
Compost 4	7.67^{a}	11.45^{a}	2.04^{a}	1.44^{a}	0.00^{a}	1.23^{a}	20.21^{a}	44.04^{a}
Compost 5	7.48^{a}	11.74^{ab}	2.24^{a}	1.57^{a}	0.98^{b}	1.28^{a}	20.05^{a}	45.35^{a}

* F1 – mobile (active) fraction, F2 – exchangeable fraction, F3 – bound to MnO_X fraction, F4 – organically bound fraction, F5 – bound to amorphic FeO_X fraction, F6 – bound to crystalline FeO_X fraction, F7 – residual fraction; ** Sum of fractions F1–F7; *** Means marked by the same letters in columns did not differ significantly at $\alpha \le 0.05$ according to the t-Tukey test.

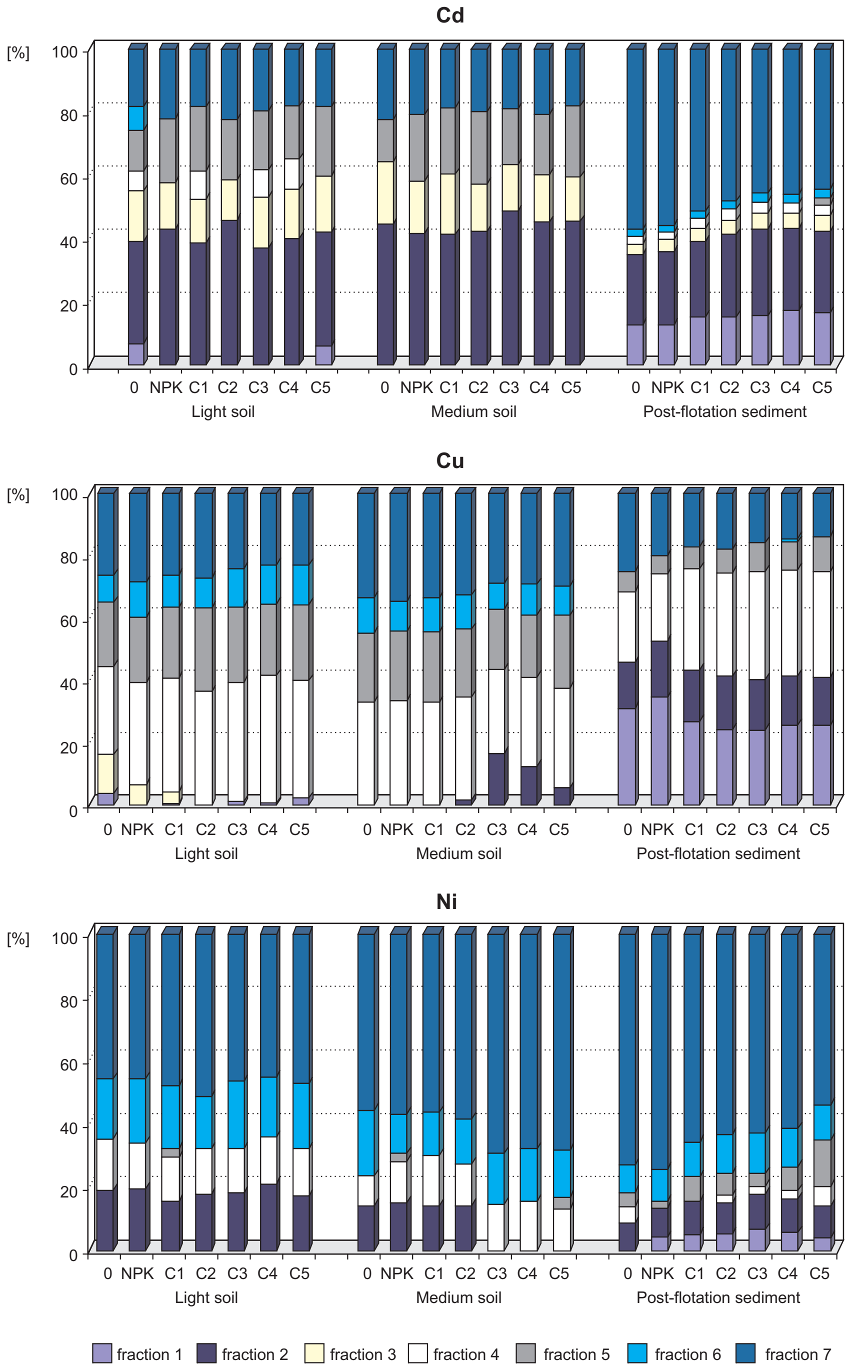

Fig. 1. Share [%] of different cadmium, copper and nickel forms in total content of metals in substrata after experiment

Only in light soil cadmium contents in: mobile (F1), bound to manganese oxides (F3) and crystalline iron oxides (F6) fractions from the non-fertilized object, and from post-floatation sediment in the residual fraction (F7), from the control and exclusively mineral treatments (1 and 2) were significantly higher than the amounts assessed in the soil from the other objects.

It was assessed that supplying composts to post-floatation sediment contributed to a reduction of residual fraction share in total amount of cadmium in comparison with mineral treatment and control (Fig. 1). The experiment confirmed the findings of other authors [8, 9] that the most mobile forms have a significant share in total cadmium content.

Summary amount of cadmium in mobile (F1), exchangeable (F2) and bound to manganese oxides (F3) fractions constituted on average 56.1 % of its total content in the light soil, 60.5 % in medium soil and 44.5 % in post-floatation sediment. However, it is worth noticing that in soils it was present mainly in the exchangeable form and bound to manganese oxides, whereas in the post-floatation sediment in mobile and exchangeable forms. Regardless of applied fertilization the dominating form of cadmium was its exchangeable form (on average 42.6 %), whereas residual fraction prevailed in post-floatation sediment revealing a very high content of this metal (on average 49.7 %).

In soil, copper is usually strongly bound to organic substance and clay minerals. On the basis of the research on the forms of copper occurrence in soil [9–12] it was established that generally the biggest amounts of this metal are bound to organic matter and amorphous iron oxides.

Fractional distribution of copper in both soils was approximate, however is significantly differed from the one determined in the post-floatation sediment (Table 3, Fig. 1). The greatest quantities of copper in soil were bound to organic matter (F4), amorphous iron oxides (F5) and to internal crystalline network of natural minerals (F7), whereas in the post-floatation sediment Cu occurred mainly in mobile and exchangeable forms (F1 and F2) and mostly in bonds with the sediment organic fraction (F4). Fertilization with different materials only slightly diversified copper content in the individual fractions. Fertilization of light soil and post-floatation sediment with composts significantly increased copper amount in organic fraction (F4) in relation to the mineral treatment and non-fertilized control. On the other hand, medium soil enrichment with composts containing polymer supplements caused that copper appeared in exchangeable form, unlike the other fertilizer combinations where no copper was found in this form.

Fertilization with composts with foil admixture also influenced a diversification among objects of single copper fractions in light soil. In the soil of these objects no copper was found in bonds with manganese oxides, whereas in soil fertilized with compost without polymer admixture, receiving mineral fertilizers or non-fertilized, copper content in this fraction ranged from 0.34 to 1.12 $mg \cdot kg^{-1}$ d.m.

A relatively considerable mobility of nickel in soil is connected with the presence of its mobile chelates, which are readily soluble, irrespectively of the pH. However, solubility of this metal bonds depends mainly on soil pH [11, 13].

Table 3

Content of different copper forms in substrates after experiment [mg · kg^{-1} d.m.]

Treatment	Content							
	F1*	F2	F3	F4	F5	F6	F7	Total**
Light soil								
Control	0.32^{c}***	0.00^{a}	1.12^{d}	2.55^{a}	1.84^{ab}	0.78^{a}	2.34^{ab}	8.96^{b}
Mineral fertilizers	0.00^{a}	0.00^{a}	0.58^{c}	2.89^{ab}	1.85^{ab}	1.00^{a}	2.50^{b}	8.83^{b}
Compost 1	0.04^{ab}	0.00^{a}	0.34^{b}	3.19^{b}	1.98^{ab}	0.92^{a}	2.26^{ab}	8.72^{ab}
Compost 2	0.00^{a}	0.00^{a}	0.00^{a}	3.07^{b}	2.28^{b}	0.82^{a}	2.27^{ab}	8.45^{ab}
Compost 3	0.08^{ab}	0.00^{a}	0.00^{a}	3.22^{b}	2.02^{ab}	1.02^{a}	2.01^{ab}	8.36^{ab}
Compost 4	0.05^{ab}	0.00^{a}	0.00^{a}	3.05^{b}	1.72^{a}	0.95^{a}	1.69^{a}	7.45^{a}
Compost 5	0.19^{bc}	0.00^{a}	0.00^{a}	3.24^{b}	2.11^{ab}	1.08^{a}	1.97^{ab}	8.60^{ab}
Medium soil								
Control	0.00^{a}	0.00^{a}	0.00^{a}	2.49^{a}	1.66^{a}	0.85^{a}	2.51^{a}	7.52^{a}
Mineral fertilizers	0.00^{a}	0.00^{a}	0.00^{a}	2.62^{a}	1.75^{a}	0.76^{a}	2.70^{a}	7.82^{a}
Compost 1	0.00^{a}	0.00^{a}	0.00^{a}	2.36^{a}	1.62^{a}	0.79^{a}	2.40^{a}	7.17^{a}
Compost 2	0.00^{a}	0.11^{a}	0.00^{a}	2.40^{a}	1.59^{a}	0.80^{a}	2.37^{a}	7.27^{a}
Compost 3	0.00^{a}	1.38^{d}	0.00^{a}	2.25^{a}	1.61^{a}	0.69^{a}	2.39^{a}	8.32^{a}
Compost 4	0.00^{a}	0.95^{c}	0.00^{a}	2.19^{a}	1.54^{a}	0.75^{a}	2.22^{a}	7.65^{a}
Compost 5	0.00^{a}	0.42^{b}	0.00^{a}	2.47^{a}	1.79^{a}	0.72^{a}	2.28^{a}	7.69^{a}
Post-flotation sediment								
Control	4.96^{bc}	2.33^{a}	0.00^{a}	3.63^{ab}	1.03^{a}	0.00^{a}	3.98^{c}	15.92^{b}
Mineral fertilizers	5.43^{c}	2.87^{a}	0.00^{a}	3.40^{a}	0.93^{a}	0.00^{a}	3.12^{b}	15.76^{ab}
Compost 1	4.12^{ab}	2.51^{a}	0.00^{a}	4.99^{b}	1.08^{a}	0.00^{a}	2.60^{ab}	15.31^{ab}
Compost 2	3.39^{a}	2.42^{a}	0.00^{a}	4.69^{abc}	1.07^{a}	0.00^{a}	2.49^{ab}	14.06^{a}
Compost 3	3.37^{a}	2.28^{a}	0.00^{a}	4.88^{bc}	1.29^{ab}	0.00^{a}	2.21^{a}	14.03^{a}
Compost 4	3.61^{a}	2.24^{a}	0.00^{a}	4.85^{bc}	1.26^{ab}	0.16^{b}	2.02^{a}	14.15^{ab}
Compost 5	3.55^{a}	2.17^{a}	0.00^{a}	4.75^{bc}	1.60^{b}	0.00^{a}	1.92^{a}	13.98^{a}

* See Table 2; ** see Table 2; *** see Table 2.

Like in case of the previously discussed elements, application of diversified fertilization usually did not cause significant differences in the content of individual nickel fractions (Table 4). Regardless of the fertilization nickel in the studied substrata occurred mainly in the hardly available forms (F6, F7) but in the post floatation sediment in the fraction most readily available to plants, *ie* mobile and exchangeable. Also in the research conducted by Filipek-Mazur et al [11] the biggest amounts of nickel were assessed in the soil in residual fraction.

Table 4

Content of different nickiel forms in substrates after experiment [mg · kg^{-1} d.m.]

Treatment	Content							
	F1[*]	F2	F3	F4	F5	F6	F7	Total[**]
Light soil								
Control	0.00^{a}[***]	0.81^{a}	0.00^{a}	0.69^{a}	0.00^{a}	0.80^{a}	1.95^{a}	4.25^{a}
Mineral fertilizers	0.00^{a}	0.81^{a}	0.00^{a}	0.61^{a}	0.00^{a}	0.86^{a}	1.92^{a}	4.19^{a}
Compost 1	0.00^{a}	0.67^{a}	0.00^{a}	0.58^{a}	0.13^{a}	0.84^{a}	2.06^{a}	4.29^{a}
Compost 2	0.00^{a}	0.75^{a}	0.00^{a}	0.60^{a}	0.00^{a}	0.71^{a}	2.17^{a}	4.24^{a}
Compost 3	0.00^{a}	0.77^{a}	0.00^{a}	0.59^{a}	0.00^{a}	0.91^{a}	1.97^{a}	4.23^{a}
Compost 4	0.00^{a}	0.84^{a}	0.00^{a}	0.59^{a}	0.00^{a}	0.76^{a}	1.81^{a}	4.01^{a}
Compost 5	0.00^{a}	0.75^{a}	0.00^{a}	0.64^{a}	0.00^{a}	0.90^{a}	2.05^{a}	4.34^{a}
Medium soil								
Control	0.00^{a}	0.91^{b}	0.00^{a}	0.60^{a}	0.00^{a}	1.33^{b}	3.57^{a}	6.42^{c}
Mineral fertilizers	0.00^{a}	1.03^{b}	0.00^{a}	0.90^{bc}	0.16^{a}	0.85^{a}	3.90^{a}	6.84^{c}
Compost 1	0.00^{a}	0.93^{b}	0.00^{a}	1.05^{c}	0.00^{a}	0.89^{a}	3.72^{a}	6.59^{c}
Compost 2	0.00^{a}	0.90^{b}	0.00^{a}	0.82^{abc}	0.00^{a}	0.89^{a}	3.68^{a}	6.28^{bc}
Compost 3	0.00^{a}	0.00^{a}	0.00^{a}	0.76^{ab}	0.00^{a}	0.83^{a}	3.58^{a}	5.16^{a}
Compost 4	0.00^{a}	0.00^{a}	0.00^{a}	0.80^{abc}	0.00^{a}	0.84^{a}	3.49^{a}	5.14^{a}
Compost 5	0.00^{a}	0.00^{a}	0.00^{a}	0.70^{ab}	0.20^{a}	0.77^{a}	3.61^{a}	5.27^{ab}
Post-flotation sediment								
Control	0.00^{a}	0.84^{a}	0.00^{a}	0.51^{c}	0.42^{bc}	0.84^{a}	7.07^{b}	9.68^{c}
Mineral fertilizers	0.39^{bc}	0.87^{a}	0.00^{a}	0.00^{a}	0.19^{a}	0.93^{a}	6.86^{b}	9.24^{bc}
Compost 1	0.41^{bc}	0.84^{a}	0.00^{a}	0.00^{a}	0.61^{c}	0.89^{a}	5.27^{a}	8.03^{a}
Compost 2	0.42^{bc}	0.78^{a}	0.00^{a}	0.19^{b}	0.55^{c}	0.96^{a}	5.04^{a}	7.95^{a}
Compost 3	0.49^{c}	0.85^{a}	0.00^{a}	0.18^{b}	0.28^{ab}	0.97^{a}	4.65^{a}	7.40^{a}
Compost 4	0.43^{bc}	0.80^{a}	0.00^{a}	0.19^{b}	0.58^{c}	0.90^{a}	4.60^{a}	7.48^{a}
Compost 5	0.34^{b}	0.83^{a}	0.00^{a}	0.53^{c}	1.21^{d}	0.93^{a}	4.50^{a}	8.34^{ab}

[*] See Table 2; [**] see Table 2; [***] see Table 2.

It is worth noticing that in both soils nickel bound to soil humus (F4) constituted a relatively big share in the metal total content. Analysis the results obtained from research conducted on the post-floatation sediment revealed that fertilization with composts contributed to a significant decrease in nickel content in the residual fraction (F7) with simultaneous increasing the number of its organic bonds (F7) in the substratum in comparison with mineral fertilization (object 2).

Conclusions

1. The contents of analysed metal forms to the greatest extent depended on the studied element and used substratum, whereas compost supplement with 8 % admixture

of various polymer foils generally had no marked effect on the distribution of metal content in the researched fractions.

2. The greatest quantities of cadmium in soils were assessed in fraction bound exchangeably, bonds with manganese oxides and residual, whereas in the post-floatation sediment in the residual fraction and bound to crystalline iron oxides.

3. Copper to the highest degree was bound to organic matter and natural minerals. Application of composts with polymer materials supplement decreased the content of mobile copper forms in comparison with mineral fertilization.

4. Nickel in the tested substrata, except for the post floatation sediment was found mainly in hardly available forms. Far greater nickel mobility was demonstrated in post floatation sediment, where considerable amounts of the metal, beside the residual fraction occurred also in mobile and exchangeable fractions.

5. No explicit effect of the kind of polymer used in composting on cadmium, copper or nickel solubility was observed.

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ROZPUSZCZALNOŚĆ METALI CIĘŻKICH W GLEBACH NAWOŻONYCH KOMPOSTAMI Z DODATKIEM TWORZYW POLIMEROWYCH

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Abstrakt: Stosowanie kompostów z odpadów komunalnych do celów nawozowych, z uwagi na dużą zawartość materii organicznej oraz składników pokarmowych, na ogół korzystnie wpływa na plon roślin i właściwości gleby. Do ich produkcji są wykorzystywane biodegradowalne frakcje odpadów komunalnych, bardzo często pochodzące ze zbiórki nieselektywnej i w związku z tym mogą zawierać pewne ilości zanieczyszczeń, zarówno organicznych, jak i mineralnych, np. metale ciężkie, które mogą negatywnie oddziaływać na żyzność gleby.

W oparciu o doświadczenie wazonowe badano wpływ kompostów z domieszką materiałów polimerowych modyfikowanych skrobią jako biokomponentem na rozpuszczalność metali ciężkich w testowanych podłożach, na których uprawiano owies i gorczycę. Komposty zastosowano do dwóch gleb o naturalnej zawartości metali ciężkich oraz gleby i osadu poflotacyjnego z przeróbki rud cynkowo-ołowiowych zanieczyszczonych metalami ciężkimi. Do nawożenia zastosowano 5 kompostów, do wytworzenia których wykorzystano substrat złożony ze słomy pszennej, rzepakowej i odpadów z czyszczenia grochu z ośmioprocentowym dodatkiem folii polimerowych różniących się między sobą udziałem skrobi oraz gęstością. Analizę specjacyjną wybranych metali ciężkich wykonano metodą sekwencyjnej ekstrakcji według Zeiena i Brümmera.

Na podstawie przeprowadzonych badań stwierdzono, że zawartość poszczególnych form metali w największym stopniu zależała od analizowanego pierwiastka oraz zastosowanego podłoża. Natomiast dodatek kompostów z 8% domieszką różnych folii polimerowych z reguły nie miał istotnego wpływu na rozkład zawartości metali w badanych frakcjach. Najwięcej kadmu w glebach oznaczono we frakcji związanej wymiennie, w formie połączeń z tlenkami manganu oraz rezydualnej, najsilniej związanej ze stałą fazą gleby. W odpadzie poflotacyjnym najwięcej kadmu oznaczono we frakcji rezydualnej oraz związanej z krystalicznymi tlenkami żelaza. Największe ilości miedzi były związane z materią organiczną oraz minerałami pierwotnymi. Stosowanie kompostów z dodatkiem materiałów polimerowych zmniejszało zawartość ruchliwych form miedzi w porównaniu z nawożeniem mineralnym. Nikiel w badanych podłożach, poza odpadem poflotacyjnym, znajdował się głównie w formach trudnodostępnych. Znacznie większą mobilność niklu wykazano w odpadzie poflotacyjnym, w którym metal ten, oprócz frakcji rezydualnej, w znacznej ilości występował we frakcjach: ruchliwej oraz wymiennej.

Słowa kluczowe: metale ciężkie, sekwencyjna ekstrakcja, gleba, osad poflotacyjny, kompost, tworzywa polimerowe

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IMPACT OF BOTTOM SEDIMENTS ON ASSIMILABILITY OF COPPER AND ZINC IN LIGHT SOIL

WPŁYW OSADÓW DENNYCH NA PRZYSWAJALNOŚĆ MIEDZI I CYNKU W GLEBIE LEKKIEJ

Abstract: The aim of the research was to evaluate an effect of bottom sediment addition on the content of soluble forms of copper and zinc in light soil as well as to evaluate the bioaccumulation of these elements by energetic plants, *ie Miscanthus giganteus* and *Sida hermaphrodita*. In order to reach the research goal, a field experiment was set up in autumn 2010 in Lipie near Rzeszow using the method of random blocks. The experimental design included 3 doses of the bottom sediment added to soil and a control treatment without sediment supplement. Doses of the bottom sediment were calculated based on soil hydrolytic acidity and the content of calcium carbonate in the sediment. The bottom sediment used in the experiment was taken from the Rzeszow Reservoir and was characterized by alkaline reaction and silt texture. Moreover, it showed an 8-times greater content of soluble forms of copper and zinc in comparison to the experimental soil. The soil of experimental field had granulometric composition of weakly clayey sand with very acid reaction ($pH_{KCl} = 4.53$), as well as low content of soluble and bioavailable forms of copper and zinc. *Miscanthus giganteus* and *Sida hermaphrodita* were chosen for test plants. In autumn 2011 and 2012, soil samples were collected from the experimental plots. In those samples, the contents of copper and zinc soluble forms extracted with 1 mol $HCl \cdot dm^{-3}$ were determined according to Rinkis method. The content of copper and zinc in soil samples and the above-ground parts of plant was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). On the basis of the obtained results, the bioaccumulation factor [BF] of both metals in the above-ground plant biomass was calculated. The obtained results were elaborated statistically using a one-way analysis of variance and Tukey's test at a significance level of $\alpha = 0.01$.

The addition of the bottom sediments to the light soil caused a change its reaction in all the experimental treatments in relation to the control treatment. The applied doses of bottom sediments did not cause exceeding the permissible concentrations of copper and zinc in the examined soil. The content of available for plants soluble forms of copper and zinc in light soil under *Miscanthus giganteus* and *Sida hermaphrodita* cultivation increased as consequence of rising bottom sediment doses introduced to the substratum. The addition of the bottom sediments to the soil resulted in a decrease of values of the bioaccumulation factor of copper and zinc in selected energetic plants.

Keywords: bottom sediments, copper, zinc, soluble forms, bioaccumulation factor

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Introduction

Sediments that are deposited at the bottom of water bodies as a result of sedimentation have a very varied chemical composition. Apart from nutrients, they also contain toxic substances that get into waters with surface flow, with industrial and municipal sewage or with inflow waters. Bottom sediments are important in the functioning of water ecosystems and constitute an integral part of the water environment [1, 2]. Bottom sediment management or disposal after their extraction from the bottom of rivers, dam reservoirs, ponds, channels or ports is currently an important ecological problem [3–5]. Agricultural use of chemically and biologically uncontaminated bottom sediments may be the most rational way of using them, as reported by many authors [3, 6–9]. It is commonly known that mineral-organic materials might be used to enrich marginal soils with assimilable minerals [7]. One of the materials might be bottom sediments, especially the ones with neutral or basic reaction and with a large amount of silt and clay fractions [9].

With relation to the above, the aim of the research was to evaluate an effect of the bottom sediment addition on the amount of soluble forms of copper and zinc in light soil, as well as on bioaccumulation of copper and zinc in energetic plant biomass.

Material and methods

The research on the effect of bottom sediment addition to light soil was conducted in the years 2011–2012 in field experiment conditions. In order to reach the research goal, a field experiment was set up in autumn 2010 in Lipie near Rzeszow using the method of random blocks. Two energetic plants, *ie Miscanthus giganteus* and *Sida hermaphrodita,* were chosen as test plants. The field experiment comprised 32 plots, with an area of 10 m^2 each. In spring 2011, *Miscanthus giganteus* seedlings were planted on 16 of them, and *Sida hermaphrodita* seedling were planted on the remaining 16 plots. Doses of the bottom sediment introduced to soil were calculated based on the content of calcium carbonate in the sediment and on soil hydrolytic acidity (Hh), *ie* doses of CaO were calculated according to a half, one and two hydrolytic acidity values.

The experimental design comprised 4 treatments (each in 4 replications) which differed in the dose of the introduced bottom sediments: I – control, II – soil + 5.625 $Mg \cdot ha^{-1}$ of sediment DM, III – soil + 11.25 $Mg \cdot ha^{-1}$ of sediment DM, IV – soil + 22.5 $Mg \cdot ha^{-1}$ d.m. of sediment. Additionally, treatments in which *Miscanthus giganteus* or *Sida hermaphrodita* were the test plants were marked with M and S symbols, respectively.

The bottom sediment used in the experiment came from the Rzeszow Reservoir and was characterized by alkaline reaction (pH_{KCl} = 7.89) as well as sandy silt granulometric composition. The contents of copper and zinc in the bottom sediment did not exceed the permissible values for output according to the Regulation of the Minister of Environment of 16 April 2002 on the types and concentrations of substances that cause the output is contaminated [10] and according to the Regulation of the Minister of Environment of 9 September 2002 on soil quality standards and earth quality standards [11]. The experimental soil had granulometric composition of weakly clayey sand and very acid reaction (pH_{KCl} = 4.53). The contents of available copper and zinc forms in soil and sediment are presented in Table 1.

Table 1

Content of assimilable forms of copper and zinc as well as pH value of soil and of bottom sediments used in the experiment

Specification	Cu	Zn	pH_{KCl}
	soluble in 1 mol $HCl \cdot dm^{-3}$ [$mg \cdot kg^{-1}$]		
Light soil	< 4	14.1	4.53
Bottom sediment	27.1	105.7	7.89

In autumn 2011 and 2012, soil samples weighing approximately 0.5 kg were collected from the experimental plots. In those samples, pH_{KCl} was measured potentiometrically, and the contents of copper and zinc soluble forms extracted with 1 mol $HCl \cdot dm^{-3}$ were determined according to Rinkis method by means of atomic absorption spectrometry (AAS).

After vegetation, in November 2011 and 2012, the above-ground biomass obtained in the experiment was gathered and homogenized using a mechanical cutter. Samples of plant material were collected from such prepared cumulative samples (from individual plots). The biomass collected in this way was subjected to dry mineralization at a temperature of 450 ^{o}C, and the obtained ash was dissolved in 20 % nitric acid. The content of copper and zinc in the above-ground parts of both test plants was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). On the basis of the obtained results, the bioaccumulation factor (BF) was calculated for the above-ground parts as a ratio of the content of copper and zinc in plant to their content in soil. The obtained results were elaborated statistically, taking into consideration a one-way analysis of variance and Tukey's test at a significance level of $\alpha = 0.01$.

Results

Total amount of the both studied elements introduced to the soil was calculated basing on the total content of copper and zinc in the bottom sediment (Table 2). The results of pH_{KCl} measured in the soil samples after harvest of *Miscanthus giganteus* and *Sida hermaphrodita* taken from individual treatments are presented in Table 2.

Table 2

Total content of copper and zinc introduced into the soil with bottom sediment and pH_{KCl} of soil

Treatments*	Cu	Zn	pH_{KCl}	
	[$kg \cdot ha^{-1}$ d.m.]		*Miscanthus giganteus*	*Sida hermaphrodita*
I	—	—	4.53	4.53
II	1.90	7.42	5.50	5.15
III	3.81	14.86	6.00	5.79
IV	7.62	29.72	6.43	6.57

* For explanations see methods.

When analyzing the soil reaction in individual treatments, it was found that addition of the bottom sediment to light soil changed the soil reaction, depending on applied dose. In the treatment where half a dose, *ie* according to 0.5 Hh, was used, soil pH was 5.50 in the case of *Miscanthus giganteus* cultivation, and pH = 5.15 when *Sida hermaphrodita* was cultivated. Addition of a full sediment dose, *ie* according to 1 Hh, improved the soil reaction (to pH = 6.0) in the treatment where *Miscanthus giganteus* constituted vegetation cover for soil, and to pH = 5.79 in the treatment with *Sida hermaphrodita*. A double sediment dose, *ie* according to 2 Hh, changed the reaction of light soil to pH = 6.43 (*Miscanthus giganteus*) and pH = 6.57 (*Sida hermaphrodita*) (Table 2).

Copper content was within a narrow range, from 2.47 to 4.81 $mg \cdot kg^{-1}$ of soil d.m. in the 1st year of the experiment, and from 1.64 to 3.47 $mg \cdot kg^{-1}$ of soil d.m. in the 2nd year of the experiment in the case of *Miscanthus giganteus* cultivation, and from 2.59 to 4.92 $mg \cdot kg^{-1}$ of soil d.m. and from 1.78 to 3.22 $mg \cdot kg^{-1}$ of soil d.m. in the 1st and 2nd year of the experiment, respectively, when *Sida hermaphrodita* was cultivated (Table 3).

Table 3

Content of soluble forms of copper and zinc in light soil

Treatments*	Years of research			
	2011	2012	2011	2012
	Cu		Zn	
	[$mg \cdot kg^{-1}$ d.m.]			
M I	2.47^{a}	1.64^{a}	9.66^{a}	9.36^{a}
M II	2.78^{a}	1.92^{a}	9.81^{a}	9.92^{a}
M III	4.12^{a}	2.73^{a}	10.82^{a}	11.66^{a}
M IV	4.81^{a}	3.47^{a}	11.14^{a}	12.74^{a}
S I	2.59^{a}	1.78^{a}	10.07^{a}	9.75^{a}
S II	3.05^{a}	2.01^{a}	10.51^{ab}	10.37^{a}
S III	3.43^{a}	2.38^{ab}	10.80^{ab}	11.32^{a}
S IV	4.92^{b}	3.22^{b}	13.98^{b}	12.60^{a}

* For explanations see methods.

In the treatment where *Miscanthus giganteus* constituted the vegetation cover, the content of soluble forms of copper increased proportionally to the increase of the bottom sediment dose in the first and second year of the experiment. Those differences were not statistically significant. The highest content of the copper soluble forms, amounting to 4.92 $mg \cdot kg^{-1}$ of soil d.m., was found in the soil on which *Sida hermaphrodita* was cultivated in the treatment where the sediment dose according to 2 Hh was applied. The smallest copper content, amounting to 1.78 $mg \cdot kg^{-1}$ of soil d.m., was stated in control without addition of bottom sediment (Table 3). It was established that the differences in copper content in the biomass of *Sida hermaphrodita* were statistically significant. The contents of the soluble form of copper in the second year of the experiment decreased on average by 32 % in treatments where *Miscanthus giganteus* was cultivated, and by 33 % in treatments where *Sida hermaphrodita* was cultivated (Table 3).

Zinc content in soil in the case of *Miscanthus giganteus* cultivation was increasing along with the increase in the bottom sediment amount added to soil, and it was, respectively: from 9.66 mg · kg^{-1} of soil d.m. in control treatment to 11.14 mg · kg^{-1} of soil d.m. in the treatment with double sediment dose in the 1st year, and from 9.36 mg · kg^{-1} of soil d.m. to 12.74 mg · kg^{-1} of soil d.m. in the 2nd year (Table 3). Zinc content in the soil in the second year of the experiment in the control treatment diminished by 3 %, whereas in treatments with addition of the sediment that content increased on average by 7 %. Those differences were not statistically significant. In the treatment where *Sida hermaphrodita* constituted the soil cover, a statistically significant diversification in soluble form of zinc contents was found and they amounted from 10.07 mg · kg^{-1} of soil d.m. in the control treatment to 13.98 mg · kg^{-1} of soil d.m. in the treatment with a double dose of the bottom sediment after the 1st year of plant vegetation, and from 9.75 mg · kg^{-1} of soil d.m. in the control treatment to 12.60 mg · kg^{-1} of soil d.m. in the treatment with the biggest dose of the sediment after the 2nd year of plant vegetation (Table 3). The soil abundance in zinc increased in the second year of the experiment only in the treatment with single dose of the bottom sediment, and in other treatments it decreased on average by 5 %, and the differences were not statistically significant (Table 3).

When analyzing the copper content in the biomass of *Miscanthus giganteus*, a small diversification in concentrations of this element can be found, ranging from 1.79 mg · kg^{-1} of d.m. in the control treatment to 2.10 mg · kg^{-1} of d.m. in the treatment with a double dose of the sediment. Similar contents were found in the biomass of *Sida hermaphrodita*, ranging from 1.80 mg · kg^{-1} of d.m. in the control treatment to 2.49 mg · kg^{-1} of d.m. in the treatment with a double dose of the sediment (Table 4).

Table 4

Content of copper and zinc in plant biomass

Treatments*	Years of research			
	2011	2012	2011	2012
	Cu		Zn	
	[mg · kg^{-1} d.m.]			
M I	1.79^{a}	1.88^{a}	31.67^{b}	44.22^{a}
M II	1.82^{a}	1.95^{a}	27.72^{ab}	37.17^{a}
M III	1.85^{a}	2.11^{a}	27.63^{ab}	35.06^{a}
M IV	1.99^{a}	2.10^{a}	26.45^{a}	35.70^{a}
S I	1.80^{a}	2.28^{a}	15.87^{b}	39.07^{a}
S II	2.06^{a}	2.32^{a}	11.56^{a}	29.53^{a}
S III	1.89^{a}	2.33^{a}	10.19^{a}	28.85^{a}
S IV	1.98^{a}	2.49^{a}	10.27^{a}	27.51^{a}

* For explanations see methods.

Results of analyses confirm the effect of bottom sediment addition on the copper content in the biomass of energetic plants increasing its level, although these differences are not statistically significant. Moreover, an increase in the copper content was found in the second year of the experiment in the biomass of *Miscanthus giganteus* on average by 7 %, and in the biomass of *Sida hermaphrodita* – on average by 18 % (Table 4). Zinc content in the biomass of *Miscanthus giganteus* in the 1st year of the experiment was between 26.45 mg · kg^{-1} of d.m. in the treatment with a double dose of the sediment and 31.67 mg · kg^{-1} of d.m. in the control treatment, and in the 2nd year of the experiment this content was between 35.06 mg · kg^{-1} of d.m. in the treatment with single dose of the sediment and 44.22 mg · kg^{-1} of d.m. in the control treatment (Table 4). The zinc content in the biomass of *Sida hermaphrodita* after the 1st year of vegetation was between 10.19 and 15.87 mg · kg^{-1} of d.m., and between 27.51 mg · kg^{-1} and 39.07 mg · kg^{-1} of d.m. after the 2nd year of vegetation (Table 4). Differences in zinc content in the biomass of *Miscanthus giganteus* and *Sida hermaphrodita* were statistically significant only in the 1st year of the experiment. It needs to be stated that the addition of half a dose of the bottom sediment to the soil caused a decrease in zinc content in the biomass of *Miscanthus giganteus*, on average by 17 %, and in the biomass of *Sida hermaphrodita* – by 34 % (Table 4). The simple and double doses of the bottom sediment addition to the soil on average influenced to a lesser degree the zinc content, lowering its concentration in the biomass of the test plants (Table 4).

Bioaccumulation factor of copper in biomass of *Miscanthus giganteus* ranged from 0.41 to 1.14, and in biomass of *Sida hermaphrodita* fluctuated from 0.40 to 1.28 (Table 5). Bioaccumulation factors for copper were decreasing along with an increase of the bottom sediment addition to the soil in both years of the experiment, as well as in the case of both cultivated test plants.

Table 5

Values of bioaccumulation factor of copper and zinc in plant biomass

Treatments*	Years of research			
	2011	2012	2011	2012
	Bioaccumulation factor [BF]			
	Cu		Zn	
M I	0.72	1.14	3.28	4.72
M II	0.65	1.01	2.82	3.75
M III	0.45	0.77	2.55	3.01
M IV	0.41	0.60	2.37	2.80
S I	0.69	1.28	1.57	4.01
S II	0.67	1.15	1.10	2.85
S III	0.55	0.98	0.94	2.55
S IV	0.40	0.77	0.73	2.18

* For explanations see methods.

The computed values of the bioaccumulation factor of zinc in biomass of *Miscanthus giganteus* varied from 2.37 to 4.72, and in biomass of *Sida hermaphrodita* ranged from 0.73 to 4.01 (Table 5). Similarly as in the case of copper, the bioaccumulation factor of zinc was decreasing along with the increase of the bottom sediment addition to the soil, regardless of the year of experiment or tested plant.

Discussion

The bottom sediment used in the field experiment had alkaline reaction, and after adding and mixing with the very acid soil used in the experiment it significantly improved soil pH and increased productivity of soil. The change in soil reaction in individual experimental treatments depended on the applied sediment dose and on calcium carbonate that was introduced along with the sediment.

According to the previously mentioned regulations, the contents of copper and zinc in the studied experimental treatments did not exceed their permissible contents for output [10], as well as for group B soil quality and ground quality [11]. With relation to the above, it is rational to utilize bottom sediment for agricultural purposes. Despite the introduction of 7.62 $kg \cdot ha^{-1}$ of copper and 29.72 $kg \cdot ha^{-1}$ of zinc (Table 2) to the soil along with the sediment, the content of assimilable forms of both these elements did not increase significantly, which can be attributed to the change in soil reaction. It is commonly known that soil reaction has high effect on metal mobility, and increase in pH value causes a decrease of solubility of copper and zinc in soil [12–15].

A small increase in the content of assimilable forms of copper and zinc in soil of treatments in which bottom sediment was used is beneficial from agricultural point of view, because it may have stimulating effect on the increase in biomass yield from cultivated energetic plants.

The value of the bioaccumulation factor (BF) determines plant sensitivity to elements and also reflects the plant capacity to uptake the element from soil, and it informs about the transfer of this metal from the soil solution to the above-ground parts of a plant and roots [16–18]. This factor is the ratio of the content of an element in a plant to its content in soil. The calculated values of bioaccumulation factors for copper and zinc showed a medium degree of accumulation (BF; 0.1–1), as well as intensive accumulation (BF; 1–10). In comparison to control treatments, the increase of the bottom sediment addition to light soil influenced the decrease in accumulation of copper and zinc in the energetic plants used in the experiment (Table 5).

In all variants that were used, the addition of the bottom sediment influenced the decrease in the bioaccumulation factor for copper and zinc in the biomass of energetic plants (Table 5). When describing the bioaccumulation factor for Cu and Zn, Kabata-Pendias and Pendias [19] stated that despite the higher copper and zinc content in a soil solution, these elements are intensively uptaken by plants. The obtained results point out to a different degree of uptake of the studied elements by the test plants, *ie Miscanthus giganteus* and *Sida hermaphrodita*. It is undoubtedly connected with the physiology of these plants and their different soil requirements.

Conclusions

1. The bottom sediment addition to the soil caused a change in light soil reaction of all experimental treatments in relation to the control treatment.

2. The content of soluble forms of copper and zinc in light soil in the case of *Miscanthus giganteus* and *Sida hermaphrodita* cultivation increased along with an increase of the bottom sediment dose.

3. The applied doses of the bottom sediment did not exceed the permissible concentrations of copper and zinc in the studied soil.

4. The bottom sediment addition to the soil caused the decrease in the value of bioaccumulation factor of copper and zinc in selected energetic plants.

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WPŁYW OSADÓW DENNYCH NA PRZYSWAJALNOŚĆ MIEDZI I CYNKU W GLEBIE LEKKIEJ

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Abstrakt: Celem badań była ocena wpływu dodatku osadu dennego na zawartość rozpuszczalnych form miedzi i cynku w glebie lekkiej oraz ocena bioakumulacji tych pierwiastków przez rośliny energetyczne, tj. *Miscanthus giganteus* i *Sida hermaphrodita*. Dla realizacji tego celu badań założono doświadczenie polowe jesienią 2010 r., w miejscowości Lipie koło Rzeszowa, metodą losowanych bloków. Schemat doświadczenia obejmował 3 dawki osadu dennego stosowanego do gleby oraz obiekt kontrolny bez dodatku osadu. Dawki osadu obliczono na podstawie wartości kwasowości hydrolitycznej gleby oraz zawartości węglanu wapnia w osadzie. Wykorzystany w doświadczeniu osad denny pobrany ze Zbiornika Rzeszowskiego miał odczyn alkaliczny oraz skład granulometryczny pyłu. Ponadto wykazywał 8-krotnie większą zawartość rozpuszczalnych form miedzi i cynku, w porównaniu z glebą użytą w doświadczeniu. Doświadczenie założono na glebie o składzie granulometrycznym piasku słabo gliniastego, o odczynie bardzo kwaśnym ($pH_{KCl} = 4,53$) oraz niskiej zawartości przyswajalnych form miedzi i cynku. Jako rośliny testowe wybrano miskant olbrzymi i ślazowiec pensylwański. Z poletek doświadczalnych jesienią 2011 i 2012 r. pobrano próbki glebowe, w których oznaczono zawartość rozpuszczalnych form miedzi i cynku ekstrahowanych 1 mol $HCl \cdot dm^{-3}$ według metody Rinkisa. Zawartość miedzi i cynku w glebie oraz częściach nadziemnych roślin oznaczono metodą atomowej spektometrii emisyjnej opartej na palniku indukcyjnie wzbudzonej plazmy (ISP-AES). Na podstawie uzyskanych wyników obliczono współczynniki bioakumulacji [WB] w nadziemnej biomasie roślin. Uzyskane wyniki opracowano statystycznie stosując jednoczynnikową analizę wariancji i test Tukeya przy poziomie istotności $\alpha = 0,01$.

Dodatek osadu dennego do gleby lekkiej spowodował zmianę odczynu gleby we wszystkich obiektach doświadczalnych w stosunku do obiektu kontrolnego. Analiza wykazała zwiększenie zawartości dostępnych dla roślin rozpuszczalnych form miedzi i cynku w glebie pod uprawą obydwu roślin testowych na skutek wprowadzenia do niej wzrastających dawek osadu dennego. Zastosowane dawki osadu dennego nie spowodowały przekroczenia dopuszczalnych zawartości miedzi i cynku w badanej glebie. Dodatek osadu dennego do gleby skutkował zmniejszeniem wartości współczynnika bioakumulacji miedzi i cynku w wybranych roślinach energetycznych.

Słowa kluczowe: osady denne, miedź, cynk, formy rozpuszczalne, współczynnik bioakumulacji

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ASSESSMENT OF SOIL BIOLOGICAL ACTIVITY UNDER CONDITIONS OF LONG-TERM DIVERSIFIED MINERAL FERTILIZATION

OCENA AKTYWNOŚCI BIOLOGICZNEJ GLEBY W WARUNKACH DŁUGOTRWAŁEGO ZRÓŻNICOWANEGO NAWOŻENIA MINERALNEGO

Abstract: Biological activity is investigated at different levels in cases of disturbances of processes, taking into consideration C and N changes in time and modern models of carbon sequestration. Soil properties created by fertilization are one of the factors influencing soil respiratory activity. This activity was measured by the manometric method in the conditions of long-term fertilizing experiment after 44 years management of the mountain meadow. One object chosen for the investigation was fertilized only with P and K and two objects were fertilized with ammonium nitrate in two doses: 90 and 180 kgN $\cdot$ ha^{-1} in the background of PK. The experiment was conducted with the limed soil and in series without liming. Manometric measurement comprised change of pressure in a closed container which was proportional to oxygen consumption and created by respiratory processes taking place in it. The equivalent amount of created CO_2 was absorbed by 1 mol $\cdot$ dm^{-3} NaOH solution. Biological activity of materials was expressed in mg$O_2 \cdot$ g^{-1} d.m. $\cdot$ d^{-1}. Equations of pressure changes indicate differences in soil respiration caused by fertilization intensification. Generally, systematic soil liming caused an increase in its biological activity. However, liming influenced this activity to a lower degree than mineral fertilization. The highest respiratory activity and dehydrogenase activity (μg TPF $\cdot$ g^{-1} f.m. $\cdot$ d^{-1}) was observed in the soil of the object fertilized with 90 kg N + PK $\cdot$ ha^{-1} and the object with fertilization increased P and K availability causing an increase in biological nitrogen fixation.

Keywords: biological activity, soil, long-term experiment

Introduction

It is considered [1, 2], that despite many factors (including moisture content or temperature) considerably affecting a temporary respiratory activity of soil, this

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indicator is a proper element describing the ecosystem metabolism. There is a strong relationship between soil respiration and the other processes occurring in it, including plant growth. In a review of the literature on the subject, Mocek-Plociniak [3] emphasizes a strong relationship between the activity of dehydrogenases and organic matter content, soil fertility, microorganism number, proteolytic activity, nitrification, denitrification, respiration, and the activities of other enzymes present in the soil environment. Generally many enzymes which belong to the dehydrogenase group produce anaerobic bacteria, therefore their intensified activity is observed under anaerobic conditions. Periodical changes of the enzyme activity are connected with changes in moisture content and soil aeration but do not depend on slight changes in C and N content in soil.

Modern models of carbon sequestration require improvement among others involving disturbances in carbon accumulation, dependencies in time of carbon and nitrogen transformations and their levels, or reactions on the border of biotic environment and substratum. On ploughlands long-term fertilization changes the soil properties and shapes plant communities. These conditions cause a change in the soil biological activity. Indirect methods of its assessment, respiration and dehydrogenase activity may be indicators of anthropopressure caused by management practices.

Material and methods

The investigations were conducted under laboratory conditions basing on the soil collected from the long-term fertilizer experiment in Czarny Potok. Soil samples from selected objects were collected in autumn 2011. The analyses were conducted in three objects (Table 1) selected from among 8 treatments managed in the experiment [4]. The object where only phosphorus and potassium fertilization was applied and objects fertilized with ammonium nitrate (90 and 180 kgN · ha^{-1} against PK) were chosen for the analyses. The experiment was conducted on the series with limed soil and without liming.

Table 1

Fertilization scheme in the static experiment in Czarny Potok

Fertilizer objects	Annual dose of the element in series 0 Ca and + Ca (1985, 1995, 2005) [kg · ha^{-1}]			Nitrogen fertilizer	Microelements
	P	K	N		
PK	39.24*	124.5*	—	—	B, Cu, Zn, Mn, Co, Mo
90 kg N + PK	39.24	124.5	90*	ammonium nitrate	B, Cu, Zn, Mn, Co, Mo
180 kg N + PK	39.24	124.5	180*	ammonium nitrate	B, Cu, Zn, Mn, Co, Mo

0 – Ca unlimed series; + – Ca limed series; * – doses of N, P and K fertilizers has been decreased by 1/3 since 2010.

A static fertilizer experiment [4], from which the soil samples were collected, has been conducted since 1968 in Czarny Potok near Krynica (20°54′53″ E; 49°24′35″ N). It is situated at about 720 m a.s.l., at the foot of Jaworzyna Krynicka Mt, in the south-eastern Beskid Sądecki Mts, on a 7^o land slope of NN exposure. The experiment was set up on a natural *Nardus stricta* L. and *Festuca rubra* type with a considerable proportion of the dicotyledonous. The soil from the experiment area was classified as brown acid soil developed from the Magura sandstone with granulometric composition of light silt loam (share of fractions: 1–0.1 mm – 40 %; 0.1–0.02 mm – 37 %; > 0.02 mm – 23 %) and characteristic three genetic horizons: AhA (0–20 cm), ABbr (21–46 cm) and BbrC (47–75 cm). The details of the experiment were presented in a previous paper [4] and in Fig. 1.

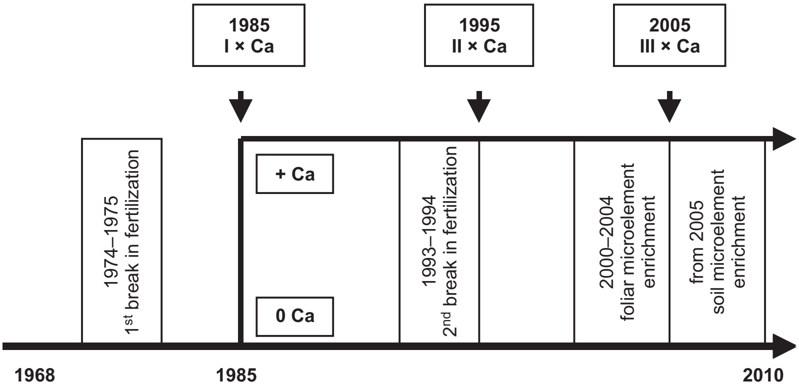

Fig. 1. Scheme of modification of cultivation measures in the experiment

Since autumn 1985 the experiment has been maintained in two series: limed and without liming, at the same level of NPK fertilization. In 1995 and 2005 liming was repeated. The lime doses for the first and third liming were calculated on the basis of 0.5 Hh value, whereas the second measure considered total hydrolytic acidity assessed in the year preceding the liming.

No mineral fertilization was applied in 1974–1975 and 1993–1994 and the investigations were limited to the assessment of the sward yield and its chemical composition.

In 1968–1980 phosphorus and potassium were sown in autumn. Since 1981 these fertilizers have been sown in spring, whereas potassium (1/2 dose) was supplemented in summer after the first cut. Thermal phosphate was used in 1968–1973, whereas triple superphosphate (46 %) has been applied since 1976 and enriched superphosphate (40 %) since 2005. Over the entire period of the experiment the nitrogen fertilizers were sown on two dates: 2/3 of the annual dose in spring when the vegetation started and 1/3 dose two weeks after the 1st cut harvesting. In 1994 10 kgCu and kgMg $\cdot$ ha^{-1} was applied once as regenerative fertilization. In 2000–2004 foliar fertilization was applied (2 $dm^3 \cdot ha^{-1}$ used twice) with Mikrovit-1 microelement fertilizer composed of 23.3 gMg; 2.3 gFe; 2.5 gCu; 2.7 gMn; 1.8 gZn; 0.15 gB and 0.1 gMo per 1 dm^3. In 2005–2007 0.5 kgB per 1 ha was applied to the soil annually, whereas in 2008 in spring 5 kgCu, Zn and Mn each per 1 ha and 0.5 kgCo and Mo each per 1 ha.

The vegetation period in the experimental area lasts from April to September (150–190 days). Meteorological conditions are variable, particularly concerning rainfall during the vegetation period. The range, after disregarding 25 % of excessive cases for annual precipitation, was from 733.2 to 990.0 mm for the years 1968–2008 and between 461.5–658.2 mm for the April–September period. Mean annual temperature was 5.86 ^{o}C.

Analysis of dehydrogenase activity was conducted in fresh soil material with natural water content. In order to determine the respiration activity collected soil material was dried in the open air and 3 weeks after collecting moistened to 30 % of maximum field moisture content. The biological activity was measured in the soil material by means of OxiTop Control measuring system [5].

Manometric measurement comprised change of pressure in a closed container (Fig. 2) which was proportional to oxygen consumption and created by respiratory processes taking place in the sample. The measurement time was 7 days and changes of respiration were registered automatically every 28 minutes (360 cycles). The equivalent amount of created CO_2 was absorbed by 1 mol · dm^{-3} NaOH solution.

Fig. 2. A photo of equipment for measuring a demand for oxygen (photo: M. Kopec)

The applied system consisted of 1 dm^3 sample bottles with equipment. For the period of measurement the sample bottles were placed in a thermostatic cabinet where the constant temperature 20 ^{o}C (±0.1 ^{o}C) was maintained. The data from the measurement were sent to the controlling head via infra-red interface and then to the computer using Achat OC programme. Biological activity of the materials was expressed in mgO$_2$ · g^{-1} d.m. of soil and computed according to the formula:

$$BA = \frac{M_{O_2}}{R \cdot T} \cdot \frac{V_{fr}}{m_{Bt}} \cdot | \Delta p |$$

where: BA – biological activity,
M_{O_2} – oxygen molecular weight (31998 mg · mol^{-1}),
R – the gas constant (83.14 L · hPa) · (K · mol)$^{-1}$,
T – measurement temperature [K],
m_{Bt} – soil dry weight [kg],
$|\Delta p|$ – change of pressure [hPa],
V_{fr} – free gas volume calculated in the following way:

$$V_{fr} = V_{ges} - VAM - VBf$$

where: V_{ges} – total volume of sample bottle,
VAM – volume of the absorber and internal auxiliary equipment,
VBf – volume of moist soil.

Soil dehydrogenase activity was measured using Thalmann [6] methodology in soil with natural moisture content. Soil samples were incubated at the temperature of 37 ^{o}C for 24 hours with 1 % solution of triphenyltetrazolium chloride (TTC) as hydrogen ion acceptor. The applied method bases on spectrophotometric measurement of triphenyltetrazolium chloride (TTC) forming in result of reduction to triphenylphormazan (TPF) at 546 nm. The result of the measurement was converted according to prepared standard curve and expressed in TPF · kg^{-1} · d^{-1}.

Regression equations and standard deviations were computed on the basis of four object replications and one-way ANOVA was conducted using Excell or Statistica programmes.

Results and discussion

In case of respiratory activity computed on the basis of regression equation in time (x) we are dealing with two equation parameters:

$$y = ax + b$$

where: a – is the change occurring in a time unit,
b – the value of reaction in the first period of incubation or its post-effect.

Table 2

Equations of pressure changes in the 2nd and 4–7th days of measurements (x = 28 – minute cycle)

Fertilising objects	2nd day	R^2	7th day	R^2
PK	$y = -0.1137x - 5.655$	0.987	$y = -0.0676x - 16.93$	0.988
PK + Ca	$y = -0.1221x - 7.403$	0.992	$y = -0.0601x - 18.951$	0.988
90 kg N + PK	$y = -0.1090x - 6.021$	0.983	$y = -0.0584x - 16.948$	0.988
90 kg N + PK + Ca	$y = -0.1141x - 7.254$	0988	$y = -0.0574x - 18.131$	0.988
180 kg N + PK	$y = -0.0907x - 5.716$	0.977	$y = -0.0547x - 14.986$	0.987
180 kg N + PK + Ca	$y = -0.0899x - 6.821$	0.981	$y = -0.0545x - 15.822$	0.989

In respect of presented results, both parameters are important. On the basis of measurements presented in Fig. 3 it was established that about the 100th cycle, which corresponds to 47th hour (the end of the second 24 hour period) of incubation a noticeable change in the respiration rate occurred.

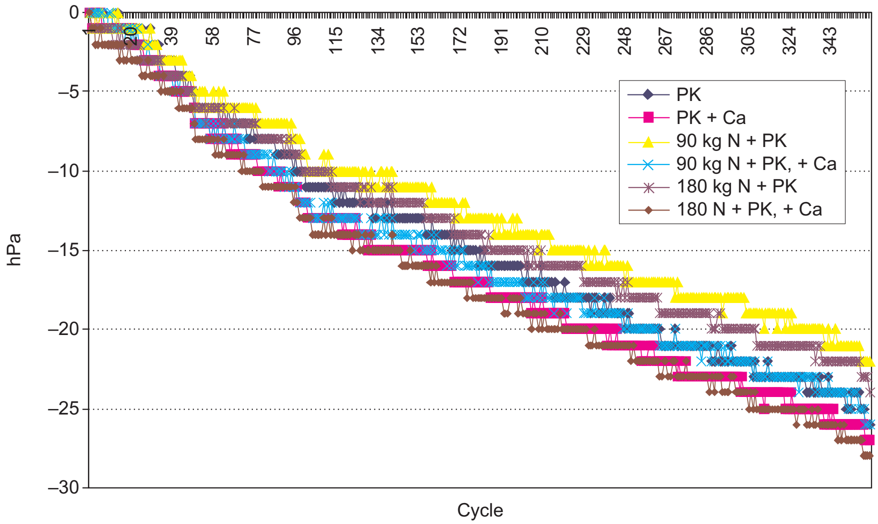

Fig. 3. Pressure changes during measurement conducted by Oxi Top Control

Table 3 presents average oxygen demand in the 2nd and 7th day of incubation and the indicator is expressed in $mgO_2 \cdot g^{-1}$ of soil d.m. and unit oxygen demand in these days converted into $mgO_2 \cdot g^{-1}$ d.m. $\cdot$ h^{-1}.

In the 24 hour period unit oxygen demand was 1.66–2 times higher than on the 7th day. On the 7th day analysis of variance revealed greater diversification of homogenous groups than on the 2nd day, what means that the test required at least four-day incubation. Homogenous groups indicate a significant effect of fertilization on respiratory activity. Marked effect of liming on this indicator was observed. Intensive fertilization with 180 kg N + PK $\cdot$ ha^{-1} led to the conditions under which the soil

Table 3

Mean daily demand for oxygen [$mgO_2 \cdot g^{-1} \cdot d^{-1}$] and respiratory activity [$mgO_2 \cdot g^{-1} \cdot h^{-1}$] in the soil in the selected periods of incubation, dehydrogenaze activity [μg TPF · $g^{-1} \cdot d^{-1}$] and soil pH

Fertilising object	Demand for oxygen [$mgO_2 \cdot g^{-1} \cdot d^{-1}$]		Respiratory activity [$mgO_2 \cdot g^{-1} \cdot h^{-1}$]		Dehydrogenaze activity		pH
	2nd day	7th day	2nd day	7th day	[μg TPF · $g^{-1} \cdot d^{-1}$]	V [%]	
PK	2.759b	9.448d	0.079	0.047	18.56b	45.99	4.71b
PK + Ca	3.396d	9.679e	0.084	0.042	17.76ab	9.78	5.31b
90 kg N + PK	2.834bc	8.935c	0.076	0.041	18.03b	11.83	4.69ab
90 kg N + PK + Ca	3.28d	9.269d	0.079	0.039	20.62b	18.23	4.85b
180 kg N + PK	2.590a	8.353b	0.063	0.038	11.59a	20.67	4.12a
180 kg N + PK + Ca	2.942c	8.087a	0.063	0.038	14.49ab	24.93	4.84b

revealed the least oxygen demand and its unit consumption in time. In case of this object, relationships between the values in soil series without liming and limed were inverted.

A similar course of variability within the object is characteristic for all objects (Fig. 4).

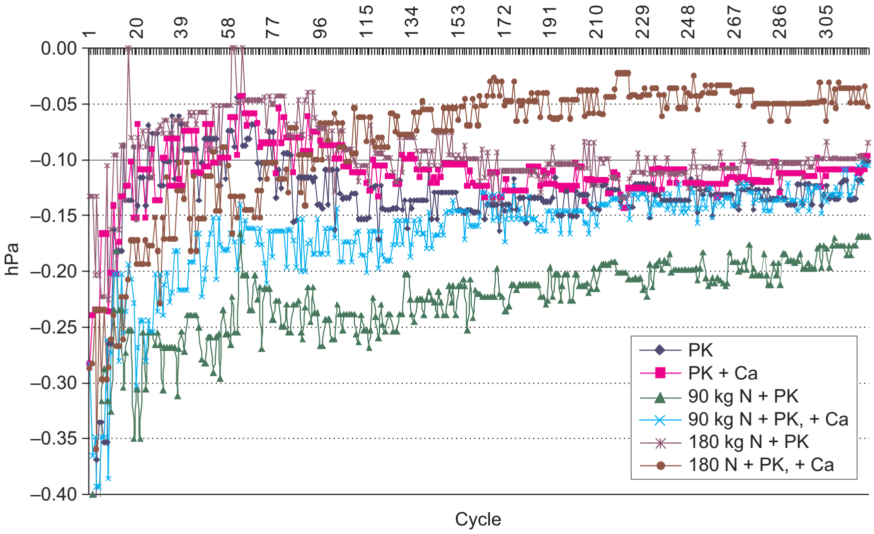

Fig. 4. Dynamics of changes of standard deviation ($n = 4$ repetitions) in comparison with arithmetic mean of pressure measurements for particular objects in the subsequent measurement cycles ($x = 28$ minutes)

In the initial phase of big changes of pressure about 50 cycles (*ie* about 1 day) the measurement became stabilized. In the final period of the analysis the variability was about 1/3 of the initial variability and was always lower within the object of the limed series. The share of deviation from 4 replications to the mean of 360 cycles in the last cycle ranged from 5 % to 17 %. The lowest variability was noted between the replications of limed series from the 180 kg N + PK object and the highest in the soil from 90 kg N + PK object.

The highest dehydrogenase activity was registered in the object fertilized with 90 kg N + PK in the limed series. In the literature [4] fertilization is regarded as optimal for maintaining the land productivity over a long period of time. Dehydrogenase activity was on a similar level in soil of both series on the object fertilized with PK and in the soil of non-limed series 90 kg N + PK. Fertilization with 180 kg N + PK caused a decline in dehydrogenase activity by 30–35 % in comparison with the soil from the corresponding objects fertilized with 90 kg N + PK. In case of nitrogen treatment in the soil of limed series, dehydrogenase activity was higher by 14–25 % than assessed in the non-limed series. The average value of dehydrogenase activity in soil of the PK fertilized object in the non-limed series was slightly divergent from the observed tendency, which might have been connected with high variability among the replication of this object.

The analysed example does not allow to show an unanimous relationship between the soil pH (Table 3) and its biological activity. Under conditions of the analysed experiment fertilization is the factor more strongly determining the values of discussed soil properties. Jiang et al [7] demonstrated that biological activity is connected with soil aggregates. It may explain presented research results, because fertilization used in the experiment modified air and water soil properties from the individual experimental objects [8]. Presented research is important for the investigations on carbon sequestration. Wang et al [9] think that in a longer perspective, soil degradation decreases sequestration on grasslands. Previous papers demonstrated that fertilization with 180 kg N + PK led to monoculture of *Holcus mollis*, shallowing of the humus horizon and depletion of some microelements [4, 8, 10]. Sakowska et al [11] revealed that among agricultural crops, the legume stand revealed a markedly better productivity and carbon dioxide use in comparison with the unicotyledonous. These conditions may arise at balancing or increasing the proportion of white clover in result of nitrogen fertilization reduction and increasing soil abundance in phosphorus and potassium.

Conclusions

1. Long-term permanent mineral fertilization caused a significant change of soil biological activity.

2. Systematic soil liming caused that its biological activity was generally bigger than when this measure was not applied. However, liming diversified this feature to a lesser extent than mineral fertilization.

3. The highest values of respiration and dehydrogenase activity were registered in the soil of the object where balanced fertilization on the level of 90 kg N + PK was used and on the object where fertilization increased abundance in phosphorus and potassium leading to better biological nitrogen fixation.

4. The analysis based on the results of measurement on 4–7 day using manometric method is a sensitive indicator of soil respiratory activity.

Acknowledgements

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OCENA AKTYWNOŚCI BIOLOGICZNEJ GLEBY W WARUNKACH DŁUGOTRWAŁEGO ZRÓŻNICOWANEGO NAWOŻENIA MINERALNEGO

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Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Współczesne modele sekwestracji węgla wymagają poznania aktywności biologicznej na różnych poziomach i przypadkach zakłócenia procesów oraz zależności przemian węgla i azotu w czasie. Jednym z elementów wpływających na aktywność respiracyjną są właściwości gleby ukształtowane nawożeniem. W warunkach długotrwałego doświadczenia nawozowego po 44 latach użytkowania górskiej runi łąkowej zbadano metodą manometryczną aktywność respiracyjną gleby. Do badań wyznaczono obiekt, w którym stosowano wyłącznie nawożenie fosforem i potasem oraz obiekty nawożone saletrą amonową w dwóch dawkach 90 i 180 kgN $\cdot$ ha^{-1} na tle PK. Doświadczenie wykonano z glebą serii wapnowanej i bez wapnowania. Pomiar manometryczny obejmował zmianę ciśnienia w zamkniętym naczyniu, która jest proporcjonalna do zużycia tlenu przez próbkę a powstaje w wyniku zachodzących w niej procesów oddychania. Powstające równoważne ilości CO_2 były absorbowane przez roztwór NaOH o stężeniu 1 mol $\cdot$ dm^{-3}. Aktywność biologiczną materiałów wyrażono w mgO_2 $\cdot$ g^{-1} s.m. $\cdot$ d^{-1}. Równania zmian ciśnienia (y) wskazują na różnice respiracji gleby spowodowane intensyfikacją nawożenia. Systematyczne wapnowanie gleby spowodowało, że jej aktywność biologiczna była na ogół większa niż w przypadku braku tego zabiegu. Wapnowanie jednak w mniejszym stopniu niż nawożenie mineralne różnicowało tę cechę. Największe wartości aktywności respiracyjnej oraz aktywności dehydrogenaz (μg TPF · g^{1} ś.m. · d^{-1}) stwierdzono w glebie obiektu, w którym stosowano zrównoważone nawożenie na poziomie 90 kg N + PK oraz obiektu, w którym zwiększono w wyniku nawożenia zasobność w fosfor i potas, powodując zwiększenie biologicznego wiązania azotu.

Słowa kluczowe: aktywność biologiczna, gleba, długotrwałe doświadczenie

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EFFECT OF FOLIAR APPLICATION OF GROWTH BIOSTIMULANT ON QUALITY AND NUTRITIVE VALUE OF MEADOW SWARD

WPŁYW DOLISTNEJ APLIKACJI BIOSTYMULATORA WZROSTU NA JAKOŚĆ I WARTOŚĆ POKARMOWĄ RUNI ŁĄKOWEJ

Abstract: The experiment was conducted during 2010–2012 on a private farm in the Slaskie province, at an altitude of 320 m above sea level. A one-factorial field experiment was set up as a randomized block design with four replications. The experimental plots, 10 m^2 in area, had class V acid brown soil. Treatment factors were spraying three concentrations (0.02, 0.04 and 0.08 %) of growth biostimulant (Tytanit fertilizer). The highest dose of the foliar application of Tytanit (0.08 %) caused significant increases in dry matter yield and nutrient content in relation to the control plot. The protein and energy value was also found to increase significantly. Satisfactory results were also obtained in plots where titanium was applied at a concentration of 0.04 %.

Keywords: meadow sward, growth biostimulant, quality and nutritive quality

In addition to basic mineral fertilizers and the application of fungicides and herbicides, increasing use in modern plant cultivation is made of a number of preparations known as plant growth regulators or biostimulants [1]. This is a relatively new group of products used to maximize yield and quality, especially under unfavourable environmental conditions for plant growth and development [2]. These preparations stimulate the development of whole plants or individual plant parts (roots, leaves); increase the rate of life processes; can make plants more resistant to stress factors; and facilitate regeneration after exposure to adverse factors. Biostimulants contribute to better seed germination and stimulate the biological activity of plants [3, 4]. Their mode

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of action makes them environmentally safe and their application helps to reduce the amount of chemicals used in agriculture and plant protection [5, 6]. Titanium is a trace element used as a biostimulant in cultivation of plants. It has a beneficial effect on the biochemical processes in plants that accelerate and enhance crop performance [7]. Titanium stimulates the activity of many enzymes, such as catalase, peroxidase, lipoxygenase and nitrate reductase. Furthermore, it accelerates metabolic processes, and facilitates the pollination, fertilization and setting of fruits and seeds [6]. Titanium increases the chlorophyll content of leaves, accelerates the growth and development of leaves, makes plants less sensitive to adverse environmental conditions, and enhances resistance to fungal and bacterial diseases [8]. Studies investigating the effect of titanium on increasing crop performance, conducted mainly with vegetables and cultivated plants, demonstrated positive effects of titanium fertilization [9, 10]. However, very few reports concern the use of titanium as a biostimulant for meadow vegetation. Therefore, the aim of this study was to determine the effect of foliar application of growth biostimulant (titanium) on the quality and nutritive value of meadow sward.

Material and methods

The field experiment, conducted during 2010–2012 on a private farm, was set up as a randomized block design with four replications. The experimental plots had class V acid brown soil with pH_{KCl} of 5.2. Abundance of available forms of potassium (111.2 $mgK \cdot kg^{-1}$ soil), manganese (52.4 $mgMn \cdot kg^{-1}$ soil) and zinc (5.6 $mgZn \cdot kg^{-1}$ soil) in the soil was intermediate, while the content of available forms of phosphorus (27.0 $mgP \cdot kg^{-1}$ soil) and copper (1.6 $mgCu \cdot kg^{-1}$ soil) was low. During the growth period (April–September), total precipitation in 2010, 2011 and 2012 was 775.1, 423.8 and 365.4 mm, respectively, with air temperatures during the same period averaging 13.1, 15.4 and 15.8 ^{o}C, respectively. The experiment consisted of four plots: a control plot (no preparation) and plots sprayed with Tytanit at the concentrations of 0.02, 0.04 and 0.08 %. The preparation was applied once for each regrowth. The first spraying was done after spring growth began and the second spraying was given after harvest during initial regrowth of sward, but not later than 3 weeks before the next cutting. During the study basic mineral fertilization was also applied: 80 $kgN \cdot ha^{-1}$ for the first regrowth, and 60 $kgN \cdot ha^{-1}$ each for the second and third regrowths in the form of ammonium nitrate. Phosphorus was applied once in the spring (120 $kgP_2O_5 \cdot ha^{-1}$) as triple superphosphate and potassium for the first and third regrowths (each at a dose of 60 $kgK_2O \cdot ha^{-1}$) as 57 % potassium salt. Each experimental plot had an area of 10 m^2. Vegetation resulted from sowing the Country 2015 mixture for extensive utilization, suitable for cutting and grazing, which contained: meadow fescue 25 %, early perennial ryegrass 10 %, intermediate perennial ryegrass 10 %, late perennial ryegrass 10 %, smooth-stalked meadow-grass 10 %, red fescue 10 %, white clover 10 %, red clover 10 %, timothy 5 %. This mixture was sown between 20 and 30 August 2009 at 40 $kg \cdot ha^{-1}$. The sward samples were analysed for chemical composition of the feed in accordance with AOAC procedure [11]. The nutritive value was estimated with the

INRA system using Winwar ver. 1.6. (DJG). The analysed plant material was evaluated using tables with nutrient ruminal and intestinal degradation data. The results were subjected to analysis of variance using Tukey's test at the $\alpha = 0.05$ level of significance.

Results

The present study showed that foliar application of different concentrations of the biostimulant (0.02, 0.04 and 0.08 %) had a significant effect on dry matter yield and organic nutrient content of meadow sward (Table 1).

Table 1

Dry matter yield and content of crude protein, crude fibre, water soluble carbohydrates (WSC), crude fat and crude ash in meadow sward

Research factors	Object	Dry matter yield	Crude protein	Crude fibre	WSC	Crude fat	Crude ash
		[dt · ha^{-1}]	[g · kg^{-1} d.m.]				
A. Growth stimulant	0	42.5	122.2	298.0	61.2	32.9	104.2
	0.02	51.2	140.9	279.0	73.9	34.6	112.6
	0.04	53.5	153.8	265.0	69.5	38.7	118.6
	0.08	60.2	179.0	256.0	67.6	39.3	123.6
	LSD$_{0.05}$	9.1	26.8	18.5	5.8	2.9	8.8
B. Year	2010	55.1	139.9	288.8	75.2	32.9	122.4
	2011	50.5	149.6	269.8	70.3	36.6	113.7
	2012	49.8	157.7	264.8	58.5	39.6	108.2
	LSD$_{0.05}$	2.0	10.3	9.2	6.9	3.1	6.3
C. Cutting	1	70.1	140.7	284.4	76.7	35.1	105.1
	2	47.3	145.1	276.6	64.4	40.4	127.9
	3	38.1	161.2	262.4	62.8	34.0	111.5
	LSD$_{0.05}$	13.4	8.2	15.0	5.1	2.5	9.6
Interaction	A × B	8.2	13.6	12.2	9.1	4.1	8.3
	A × C	ns	ns	ns	ns	ns	ns
	B × C	5.1	ns	ns	ns	ns	ns
	A × B × C	ns	ns	ns	ns	ns	ns

The biostimulant had a positive effect for all fertilizer treatments. Dry matter yield was lowest in plants from the control plot (42.5 dt · ha^{-1}) and significantly higher in plots where titanium was applied at rates of 0.04 % (53.5 dt · ha^{-1}) and 0.08 % (60.2 dt · ha^{-1}). The increasing levels of foliar fertilization with the biostimulant also significantly increased the crude protein content compared to the control plot. Best results, significantly better than others, were obtained when using the highest Ti concentration of 0.08 %. The highest titanium concentration proved most efficient when meadow sward plants were fertilized. The lowest titanium concentration had no significant effect on most of the parameters studied. No significant difference was also observed in nutrient content between the plots treated with 0.04 % and 0.08 % Ti.

During the years of the study, the average dry matter yield of harvested plants ranged from 49.8 dt · ha^{-1} (2012) to 55.3 dt · ha^{-1} (2010) with a statistically significant difference. Analysis of nutrients in different years of the study revealed that the average crude protein content of meadow sward ranged from 139.9 (2010) to 157.7 g · kg^{-1} d.m. (2012) with a statistically significant difference. The present study confirmed an inverse relationship for the content of crude protein and crude fibre. Crude fibre was highest in 2010 and lowest in 2012. A similar relationship was also noted for water soluble carbohydrates and crude ash. In turn, the content of crude fat in meadow sward plants increased in each year of the study. As regards regrowth harvests, dry matter yield was lowest in the third cutting and highest in the first. The crude protein and crude ash content of the plants was lowest for the first cutting and significantly higher for the second and third cuttings. As regards crude fibre and water soluble carbohydrates, the concentration of these nutrients was highest in the first cutting but declined in the next cuttings. A significant interaction was observed between the year of the study and foliar fertilization.

The increasing concentration of the growth biostimulant caused a significant increase in energy value (UFL from 0.65 to 0.76 g · kg^{-1} d.m., UFV from 0.55 to 0.68 g · kg^{-1} d.m.) and protein value (51–76 for PDIN and 67–81 g · kg^{-1} d.m for PDIE) (Table 2).

Table 2

Nutritive value of meadow sward

Research factors	Object	Content in 1 kg feed d.m.			
		UFL	UFV	PDIN [g]	PDIE [g]
A. Growth stimulant	0	0.65	0.55	51	67
	0.02	0.74	0.65	65	77
	0.04	0.75	0.66	78	81
	0.08	0.76	0.68	76	81
	$LSD_{0.05}$	0.04	0.04	10.7	4.6
B. Year	2010	0.71	0.63	65	75
	2011	0.72	0.63	68	77
	2012	0.74	0.64	72	80
	$LSD_{0.05}$	0.01	0.01	3.7	2.6
C. Cutting	1	0.68	0.58	62	67
	2	0.74	0.66	71	81
	3	0.75	0.66	70	82
	$LSD_{0.05}$	0.03	0.03	3.4	5.4
Interaction	A × B	0.015	0.011	4.9	3.4
	A × C	ns	ns	ns	ns
	B × C	ns	ns	ns	ns
	A × B × C	ns	ns	ns	ns

Climatic conditions in particular years had a significant effect on the feed unit values of meadow sward. All the analysed indices of nutritive value increased in each year of the study. Also the nutritive value of sward was higher in successive cuttings.

Discussion

The positive effects of foliar fertilization of plants on yield level and quality were reported by many authors [10, 12–14]. According to Faber et al [12], the beneficial effect of foliar fertilization is due, among others, to stimulating the plant's metabolism, which increases nutrient intake by the root system. Foliar fertilizers that contain macro- and micronutrients increase yields, improve plant health and even reduce damage caused by diseases and plants [15]. One of the micronutrients that stimulates plants is titanium. This element stimulates the pollination and setting of fruit and seeds, enhances resistance to fungal and bacterial diseases, accelerates the growth and development of leaves, and acts as a catalyst to improve the uptake of nutrients from the soil and foliar fertilizers [16]. According to Grenda [8], the stimulatory action of titanium is due to the increased activity of iron ions, which increases the synthesis of assimilation pigments. In another study [17], the co-author of this experiment observed increased chlorophyll content of timothy leaves in response to titanium fertilization. Titanium ions also contribute to higher enzymatic activity and better nutrient intake from the soil solution [9]. In her study, the same author obtained vegetative growth of tomato plants in response to spraying with Tytanit. This stimulant increased plant height, stem diameter, and number of leaves per plant, which resulted in higher total yield and marketable yield of tomato fruits. In practice, growth stimulants are mostly used in the cultivation of vegetables, fruits and flowers [18, 19]. Szewczuk and Juszczak [20] reported a 30 % increase in the yield of the common bean in response to Tytanit. Research with apple trees, maize, sugar beets and yellow lupin also confirms that titanium has a positive effect by increasing yields by around 10–20 % [21]. Janas et al [22] showed a significant effect of Tytanit on yielding of aubergine, particularly under adverse climatic conditions. In the present study, the years 2011 and 2012 were identified as dry years because the growth periods were characterized by considerably lower total precipitation compared to 2010. The current study demonstrated that the application of titanium reduced the adverse effects of drought on the nutrient content of meadow sward. Our experiment shows that the quality of roughages can be improved by titanium fertilization of meadow sward. This issue is of great significance on the national level. Brzoska and Sliwinski [23] reported that the quality of roughages from grasslands in Poland is inferior to that of feeds from France, for example. The differences may reach 15–20 %. The main reason is insufficient and improper fertilization. Therefore, studies aimed at improving the quality of feeds are fully justified.

Conclusions

1. The application of additional foliar fertilization with Tytanit in three different concentrations had a significant effect on nutrient content. Compared to the control plot, a 0.08 % concentration of Tytanit contributed the most to increasing the concentration of nutrients. Satisfactory results were also obtained when the preparation was sprayed at a concentration of 0.04 %.

2. Foliar application of titanium at 0.04 and 0.08 % increased the average content of desirable nutrients, but the differences between these fertilizer treatments were statistically non significant. The highest nutritive value was observed in plots where titanium was applied at 0.08 %.

3. Under adverse atmospheric conditions, Tytanit preparation showed antistress activity and contributed to increases in crude protein content, crude fat content, and protein and enzymatic value.

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WPŁYW DOLISTNEJ APLIKACJI BIOSTYMULATORA WZROSTU NA JAKOŚĆ I WARTOŚĆ POKARMOWĄ RUNI ŁĄKOWEJ

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Abstrakt: Doświadczenie polowe prowadzono w latach 2010–2012, w indywidualnym gospodarstwie rolnym w województwie śląskim, na wysokości powyżej 320 m n.p.m. Jednoczynnikowe doświadczenie polowe założono metodą losowanych bloków, w czterech powtórzeniach, powierzchnia poletek doświadczalnych wynosiła 10 m^2. Na polu doświadczalnym występowała gleba brunatna kwaśna, zaliczana pod względem bonitacyjnym do klasy V. Czynnikiem doświadczenia był oprysk biostymulatorem wzrostu w postaci nawozu Tytanit w trzech stężeniach: 0,02, 0,04 i 0,08 %. Zastosowanie nawożenia dolistnego Tytanitem w najwyższej dawce (0,08 %) spowodowało istotny wzrost plonów suchej masy oraz zawartości składników pokarmowych w stosunku do obiektu kontrolnego. Ponadto stwierdzono, również istotny wzrost wartości białkowej i energetycznej. Zadowalające efekty uzyskano także w obiektach, gdzie aplikowano tytan w stężeniu 0,04 %.

Słowa kluczowe: ruń łąkowa, biostymulator wzrostu, jakość pokarmowa, wartość pokarmowa

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ACCUMULATION OF ZINC IN SOIL IN METAL INDUSTRY AREA

AKUMULACJA CYNKU W GLEBACH TERENU ZAKŁADU PRZEMYSŁU METALOWEGO

Abstract: The metal industry area in Zielona Góra was tested, which has been functioning continuously since 1876. In the samples taken in the years 2009 and 2010 the chemical and physico-chemical properties of the soils were identified. Zinc was found in amounts between 321–3290 mg · kg^{-1}, with an average of 1340 mg · kg^{-1}. It clearly shows an anthropogenic rise in comparison to the other parts of the urban area under research – from 11 to 110 times. These values are also higher in comparison to the average content of zinc found in soils in Poland – 30 mg · kg^{-1}. Different contents of zinc were found on the premises of the plant, which depended on the location of a particular place in the relation to the production halls and other elements of the plant's infrastructure.

Keywords: zinc, soil, metal industry

Introduction

Industrial activity is one of the most important factors increasing the content of trace metals in the natural environment. A particularly high content of heavy metals is observed in soils exposed to a long-term risk of anthropopressure.

Zinc is one of the most mobile metals in the soil, affecting its overall content and different forms. Zinc undergoes soil sorption, which depends on the pH. At the pH of 5.5 it is bound by humic acids, whereas at a lower pH the sorption of this element almost completely disappears. In soils enriched with iron and manganese it is strongly absorbed on the surface of their oxides and hydroxides. Its concentration in ferruginous soil concretions nodules may reach the level of 2500 mg · kg^{-1}, and in manganese concretions 5500 mg · kg^{-1} [1].

The bioavailability of zinc in soil depends on its form, which is affected by the pH, temperature and oxidation-reduction potential and on soil sorption, solid phase capacity to exchange cations, competition with the other ions and the composition and quality of

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the soil solution [1–4]. Zinc is a trace element necessary for the development of plants, animals and humans, but in high concentrations causes a serious threat to the biosphere [5–7]. A content of about 100 mg $\cdot$ kg^{-1} of zinc in the soil may limit processes of nitrification and the presence of about 1000 mg $\cdot$ kg^{-1} causes harm to a majority of microbiological processes [8]. A reduction in the toxicity of zinc can be achieved by the treatment of the soil with lime, the addition of phosphate or sulfur compounds. Also, hydrated oxides of iron and manganese tend to hinder the process of zinc absorption by plants, which is equivalent to decreasing phytotoxicity [1]. In subject literature the negative effect of zinc on the populations of soil invertebrates is extensively described [9–14].

The main source of zinc in urban industrial and communication areas is human activity. Higher concentrations are observed in the soil near places of mining activities, foundries and steel mills, pipelines, industrial establishments and near busy thoroughfares – from emissions [15, 16]. The phenomenon of zinc accumulation in soils in the areas described is caused by the sedimentation of dust from the air.

The main source of industrial emissions of zinc into the environment are steel mills and foundries of metal and its alloys, created by the metallurgical industry. The main industrial sectors using zinc include the metal industry (used as an anti-corrosion agent and to the galvanization) and tinctorial industry. A major source of pollution are combustion processes of coal, but on the global scale they are approximately 10 % of the total emissions of this metal [1].

The aim of this study was to analyze the content of zinc in the soils of industrial area as an indicator of the long-term pressure of industrial activities on the natural environment.

Materials and methods

Description of the research object

The research object is the metal industry area located in Zielona Góra, which occupies about 11.5 acres, located in Sulechowska Street. Industrial activities in that area started in 1876. The activities involved the production of agricultural machinery, steel structures of industrial halls, bridges and railway stations. In 1886, the construction of railway freight and passenger carriages, tanks, mail carriages, refrigerated carriages, etc. During the Second World War the factory produced vehicles and equipment for the army. It produced armored trains, cannon parts, military vehicles, submarine hulls, aircraft parts. After 1945 it produced rolling stock, freight carriages and locomotives, but also steel structures [17, 18]. Currently the site produces rolling stock and steel structures. Currently in the industrial area rolling stock and steel structures are produced, part of the area is a repository of files and magazines.

The area under research is located a short distance from the city center, it is surrounded by residential buildings and single and multifamily ones to the north there is an area of greenery.

The area of industrial plant under construction was subjected to leveling. This kind of work still continues, traditionally with the use of waste materials, although in smaller quantities than before.

Research methods

Soil samples were taken from the metal industry area described in the years 2009 and 2010. Samples were collected in accordance with the provisions of the standards ISO 10381-1:2008, ISO 10381-2:2007 and ISO 10381-5, specifying how samples should be obtained for laboratory tests.

The industrial area was divided into 10 sub-surfaces from which aggregate samples with a disturbed structure were collected. Within each test area dozens of individual samples were collected to receive a bulk sample weighing about 1 kg. The places of soil sampling are shown in Fig. 1.

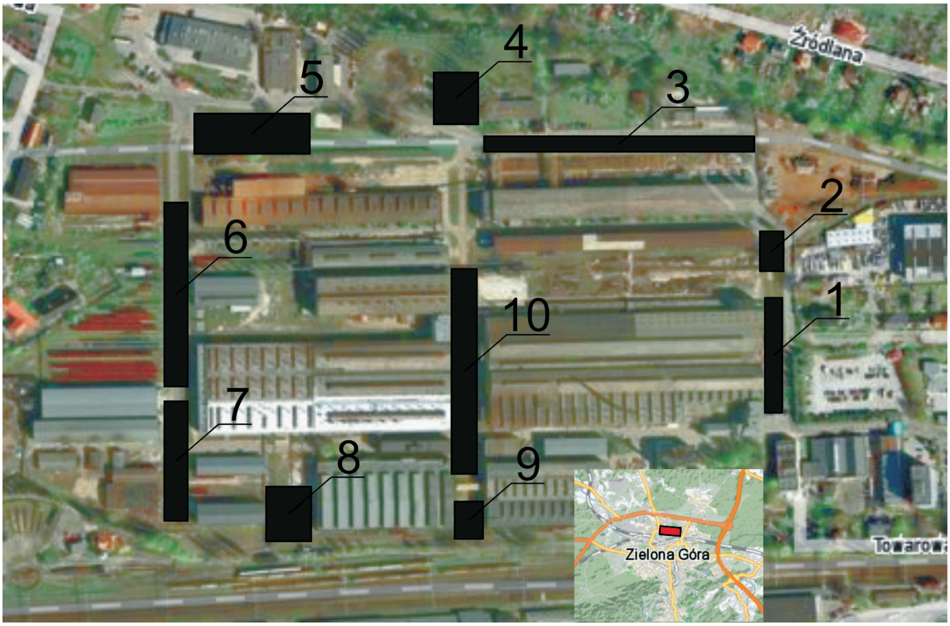


Fig. 1. Location of sampling points in the industrial area (photo: Fruzińska 2011 on undercoat Zumi.pl)

The samples collected were dried and sieved through a sieve with a diameter of 2 mm. The following tests were performed on the resulting material:

– determination of zinc in the soil in a subtotal form – atomic absorption spectrometry (AAS FL) after ignition of samples in a muffle furnace at 550 ^{o}C to constant mass and dissolving the residue after ignition in a mixture of hot concentrated acids HCl: HNO_3 relative 3 : 1 (aqua regia) according to the standard PN-ISO 11466:2002.

While previous studies performed:

– analysis of mechanical composition – areometric method by Casagrande in the modification of Proszynski, according to the standard ISO 11277:2009,

– indication of pH – according to the standard ISO 10390:2005, in water and 1-molar KCl,

– determination of manganese and iron in the soil in a subtotal form – atomic absorption spectrometry (AAS FL) after ignition of samples in a muffle furnace at 550 ^{o}C to constant mass and dissolving the residue after ignition in a mixture of hot concentrated acids HCl: HNO_3 relative 3:1 (aqua regia) according to the standard PN-ISO 11466:2002,

The analytical results underwent the Pearson correlation analysis. Correlation calculations were carried out by means of Statistica StatSoft 10 software.

Results and discussion

The content of zinc in the soils from the area under research compared with their pH, granulometric composition and the content of manganese and iron is shown in Table 1.

Table 1

The content of zinc, manganese, iron as well pH and sand content in the analyzed soil samples

Field number	Sampling series	Zinc content in soils [mg · kg^{-1}]	Manganese content in soils [mg · kg^{-1}]	Iron content in soils [mg · kg^{-1}]	pH-H_2O	Sand content 2–0.05 [%]
1	a	n.d.	n.d.	n.d.	n.d.	n.d.
	b	1360	1670	57900	7.1	95
2	a	n.d.	n.d.	n.d.	n.d.	n.d.
	b	409	162	7887	7.1	95
3	a	444	469	27700	8.0	94
	b	421	443	26600	7.4	93
4	a	364	311	10600	7.9	93
	b	435	319	14100	7.3	96
5	a	412	360	18000	7.8	92
	b	321	328	15200	7.2	93
6	a	644	774	30300	8.2	92
	b	511	510	17000	7.2	96
7	a	3290	651	47200	8.0	89
	b	2910	731	55500	7.1	91
8	a	2980	1160	57000	8.0	92
	b	2440	1690	57520	7.2	91
9	a	1660	917	54800	7.7	86
	b	2420	1200	51700	7.3	94
10	a	n.d.	n.d.	n.d.	n.d.	n.d.
	b	1800	750	48900	7.5	94
Basic statistics						
Mean		1340	732	35171	7.5	93
Minimum		321	162	7887	7.1	86
Maximum		3290	1690	57900	8.2	96
Standard deviation		1090	462	19148	0.4	3

n.d. – no determined; a – samples taken in June 2009; b – samples taken in June 2010.

The concentration of zinc in the soils from the industrial area was high and ranged from 321 mg · kg^{-1} (in the sample 5b) to 3290 mg · kg^{-1} (in the sample 7a). The average content of zinc in uncontaminated sandy soils in Poland is 30 mg · kg^{-1} [1]. Therefore, the content of zinc in the soils from the area uner research is from 10.7 to 109.6 times greater than the index. This illustrates the intensity of the transformation of this area.

The results obtained in terms of the content of zinc divided the area under research into two sectors. Values above 1000 mg · kg^{-1} were characteristic of the areas directly adjacent to the production halls. These are the places identified as 1, 7, 9 and 10. In these areas there is an overhead railway line to transport elements manufactured between different halls in the technological cycle. Also, a high content was characteristic of area No. 8 – car park. A high concentration of zinc in the soil taken for testing from this area may be due to the content of zinc in the waste materials used for leveling the ground. In areas designated as 2, 3, 4, 5, 6 a lower content of zinc may be due to the less intensive use of these places during manufacturing operations.

The maximum concentration in sample No. 7a – 3290 mg · kg^{-1} significantly exceeded the permissible content of zinc in industrial soils, which is defined in the Directive of the Minister for the Environment on standards for the quality of soil of 9 September 2002. It specifies the permissible value of zinc in the industrial soils of group C – industrials areas, the premises of mines and communications areas at the depth of 0–2 m below the surface at the level of 1000 mg · kg^{-1}.

The content of zinc in soils is influenced by many forms of human activities, and its sources may have overlapping interactions areas. While examining the industrial area situated among the buildings and surrounded by busy roads it should be remembered that the presence of zinc in the soils of such areas may be the result of not only industrial activities but also intensive traffic, railway traffic and fossil fuel combustion.

Table 2 summarizes the results for zinc in the soils of the area under research compared with other locations in Zielona Gora [19].

Table 2

The average content of zinc in the soils under research compared with the content of zinc in the soils of the town of Zielona Gora [19]

Designation	Zn [mg · kg^{-1}]	pH-H_2O	Mechanical composition
Centrum[a]	143	6.5	gravelly sand
Os. Piastowskie[b]	127	7.1	gravelly sand
Makrownętrzne Gęśnika[c]	375	7.2	gravelly sand
Dolina Zielona[d]	30	7.7	gravelly sand
This study Mean ± S.D.*	1340 ± 1090	7.5 ± 0.4	gravelly sand

* – S.D. – standard deviation; [a] – Zielona Gora, a park in the city center, post brown regosol (0–30 cm); [b] – Zielona Gora, a housing estate green area, anthropogenic soil with an undeveloped profile (0–20 cm); [c] – Zielona Gora, a house garden, near Zrodlana Street, hortisol (0–40 cm); [d] – Zielona Gora, a pile of shoveled soil material, anthropogenic soil with an undeveloped profile (0–20 cm).

A comparison of the results of the research indicates a significant concentration of this element in the soils of the industrial area. Among the areas analyzed two are located in the vicinity of the area under research. The first of them – the "Zielona Dolina" estate (situated east of the area under research), is characterized by the presence of zinc in the soils at the level of 30 mg · kg^{-1} – comparable with the content in uncontaminated sandy soils. The second, "Makrownetrze Gesnika", situated north the factory premises was characterized by a relatively high content of zinc – 375 mg · kg^{-1}. The reasons for this phenomenon are not quite clear, due to the different historical forms of using those grounds, including the intensively fertilized allotments. The other two samples, taken at the Centre and the Piaskowskie estate, were characterized by an intermediate content of zinc, but similar to values reported in subject literature [20–22].

The researched showed that in the soils of the industrial area there are significant amounts of zinc, and the level of this element varies significantly from the content in the soils in Zielona Gora located both near and further away from the plant.

In order to compare the results of the research on zinc to the results obtained elswhere in the world it is necessary to pay attention to the specific conditions prevailing in each industrial area, often not to be found anywhere else.

Table 3

The zinc content in soils of industrial and urban areas of the world

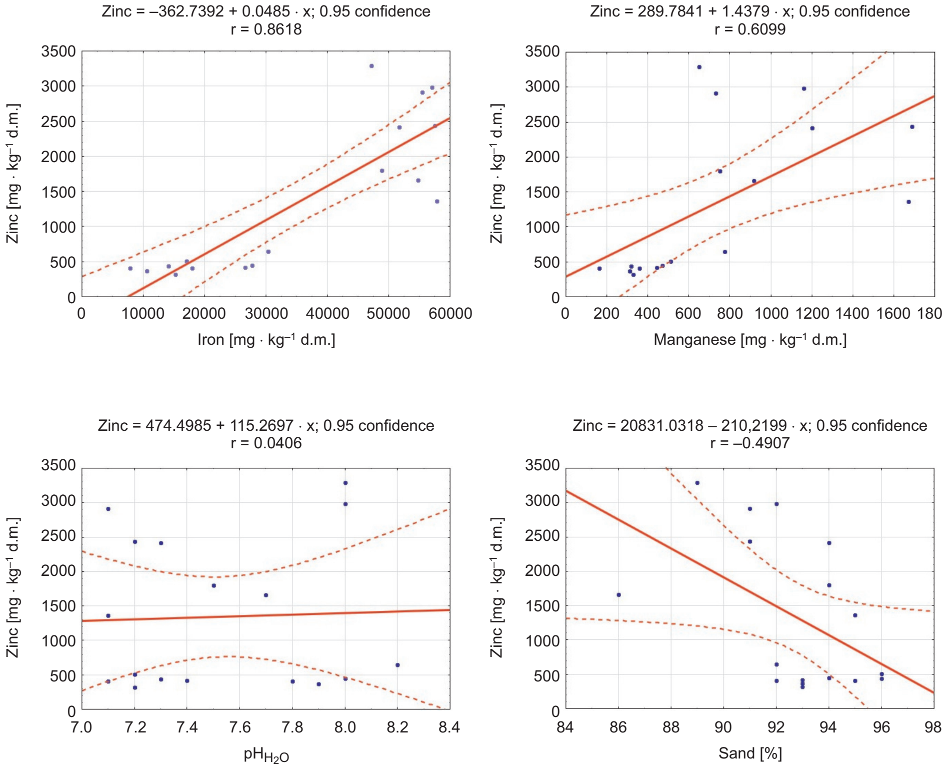
City	Zn [mg · kg^{-1}] Mean ± S.D.	Comments
Industrial areas		
Hyderabad	812 ± 1360	[23]
Kosaya Gora	276 ± 44	[24]
Hangzhou	346 ± 314	[25]
This study	**1340 ± 1090**	
Urban areas		
London	183	[21]
Glasgow	207	[20]
Hongkong	168 ± 75	[22]
Bangkok	118 ± 185	[26]
Hamburg	516 ± 680	[27]
Manila	440 ± 618	[28]

This is due to the kind of industry, raw materials used for production, technologies, climate conditions, duration of industrial activities in areas under research, and other local conditions. Even in areas that are occupied only by metal and metallurgic industry establishments, a very different zinc content in soils can be observed. In comparison with the results of tests for this group of plants, the soil in the area under research shows a much higher concentration of zinc, comparable to the value of the Balanagar industrial area, near the city of Hyderabad in India – 1340 ± 1090 mgZn · kg^{-1} in the soils of the area under research to 812 ± 1360 mgZn · kg^{-1} in the soils around the Balanagar industrial area. In addition the difference between the average values may be due to the reasons mentioned above, the choice of sampling sites.

A significant difference between the content of zinc in soils in areas of the metal industry and urban areas can be seen. These points clearly to the industry as an important local source of soil enrichment in zinc.

For the analysis of the relationship between concentrations of trace metals and the percentage content of sand the Pearson correlation is used and the results are presented in the following figures. The results obtained indicate a significant positive correlation between Zn-Fe and Zn-Mn. The correlation coefficient Zn-Fe was 0.8518 and Zn-Mn was 0.6099. A positive correlation between zinc and manganese and iron indicates the origin of these elements from a common source, from industrial pollution. The presence of iron and manganese in large quantities in soils with an alkaline pH and their high positive correlation as confirmation of their anthropogenic origin is also reflected in the results of other researches [29, 30].

Statistical calculations demonstrated that there was a significant negative correlation between the content of zinc and the granulometric composition of soils. A correlation coefficient of Zn-Sand was –0.4906. It indicates a decreasing amount of zinc with an increasing percentage of sand in the soil.



Zinc = –362.7392 + 0.0485 · x; 0.95 confidence
r = 0.8618

Zinc = 289.7841 + 1.4379 · x; 0.95 confidence
r = 0.6099

Zinc = 474.4985 + 115.2697 · x; 0.95 confidence
r = 0.0406

Zinc = 20831.0318 – 210,2199 · x; 0.95 confidence
r = –0.4907

Fig. 2. Scatterplot of Zn-Fe, Zn-Mn, Zn-pH-H_2O and Zn-Sand

A statistical analysis showed no significant correlation between the pH of the soils and the content of zinc. This is due to fact that the zinc in the test samples appeared in different concentrations, and the pH differed slightly. The pH of the test samples according to data from subject literature has an influence on the sorption of zinc [1, 31]. However, in the soil situation under research this correlation cannot be confirmed.

The high accumulation of zinc compounds in industrial areas surrounded by urban areas (including residential areas) may pose a risk of migration of this element to the soil outside the industrial area. This can occur when pollution is carried by wind and by migration into the depths of soils profiles – into groundwater. Potential environmental risks posed by a higher content of zinc in the soil should be controlled through the constant monitoring of the soil, water and plants in the selected locations.

Conclusion

1. The content of zinc in soils of the industrial area was very high and exceeded the content of zinc in urban soils in Zielona Gora, the world's urban areas and some industrial areas.
2. The concentration of zinc in soils depended on the location of sampling.
3. The zinc content in soils was strongly positively correlated with the content of iron, manganese, negatively with the percentage content of sand. The research did not indicate the concentration of zinc from the pH of the soils.
4. The high concentration of zinc in the soils under research was caused by the activity of the metal industry.

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AKUMULACJA CYNKU W GLEBACH TERENU ZAKŁADU PRZEMYSŁU METALOWEGO

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Abstrakt: Badaniom poddano obszar przemysłu metalowego w Zielonej Górze, stale funkcjonujący od roku 1876. W próbkach pobranych w latach 2009 i 2010 określono właściwości chemiczne i fizyczno-chemiczne. Stwierdzono obecność cynku w granicach 321–3290 mg · kg^{-1} ze średnią 1340 mg · kg^{-1}. Wskazuje to wyraźne antropogenne podwyższenie względem innych terenów badanego ośrodka miejskiego – od 11 do 110 razy. Jest to także wartość wyższa w odniesieniu do średniej zawartości cynku, spotykanej w glebach Polski – zawartość 30 mg · kg^{-1}. Odnotowano zróżnicowanie zawartości cynku na terenie zakładu, co jest zależne od ulokowania względem hal produkcyjnych i innych elementów infrastruktury zakładu.

Słowa kluczowe: cynk, gleba, przemysł metalowy

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METHODS OF LIQUID BIOFUEL PRODUCTION – THE BIOETHANOL EXAMPLE

METODY PRODUKCJI BIOPALIW CIEKŁYCH NA PRZYKŁADZIE BIOETANOLU

Abstract: Ethanol is used in chemical and food industry, mainly either in the synthesis or as a solvent. The newest application of ethanol is as a fuel. This alcohol, produced on an industrial scale from crop waste, is widely known under the name bioethanol. It could be used as a fuel by itself or in a mixture with gasoline. Today, there are several technologies for bioethanol production known. The relatively simple method of obtaining bioethanol is through the mechanism of fermentation. There is an interest in use and improvement of this and other production mechanisms. Given the increasing demand for alternative fuels, ethanol today is one of the most supported research and implementation issues in the fuel sector. This paper summarizes the current knowledge on the subject. In this article, data from the largest producers of ethanol in the world and an analysis of use of biofuels in each country are presented. Identified characteristics of bioethanol production and its mechanism for the main technologies of production are presented. The paper contains a forecast on the future use of biofuels – the construction of a new generation of biorefineries.

Keyworlds: biofuels, bioethanol, technology of production

Introduction

Ethanol is used in chemical and food industry, mainly in the synthesis or as a solvent. Its relatively new application is utilizing as a liquid fuel. In this case, the popular solution is to use ethanol as a supplement of gasoline, because of the fact that the pure ethanol can be used in specially modified engines. Bioethanol has excellent oxidizing properties, causes limited emission of toxic gases (such as carbon and nitrogen oxides) and increases the fuel's octane number. On the other hand, if we use addition of ethanol, it is necessary to use others compounds. They reduce its volatility and limited tribological properties of the fuel, in order to counteract increased friction and rapid wear of the engine [1].

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Ethanol can be produce from crops containing both monosaccharides and polysaccarides. In Poland, the most amount of ethanol is derived from potatoes and ryes. In future ethanol could be made from cellulosic materials, especially waste materials [1]. Production of bioethanol is still developing, the main direction of research aims at developing new techniques, lowering productions costs, lowering environmental pollutions, activation of agriculture, and, in a larger scale, reduction of oil import.

Poland has a considerable amount of excess biomass and experience in ethanol production. However, there's a problem with insufficient amount of the existing distilleries and spirit plants. Therefore, thinking about the future use of ethanol as a fuel, requires construction of new plants.

The world production of ethanol

Today the world production of ethanol is about 106 mln m^3 (83 mln tons) and have been increased by 45 % form 31–33 mln m^3 (24.5–26 mln tons) in 2004. The 93 % of this production is generated by alcohol fermentation, the rest through chemical synthesis. The main part of production is located in Brazil and USA (75 %). In Asia, the percent of production is about 18 % and in Europe – 7 %. According to statistic data from 2011 ethanol production in Poland reached 0.16 mln m^3(0.13 mln tons), which was 0.15 % of the world total production [2]. Nowadays, production of ethanol as a fuel covers 2/3 of total world production. In Brazil, 95 % of ethanol in circulation is utilized in form of fuel, in USA over 60 %, in EU only 5 %. Main European companies producing ethanol have been presented in Table 1.

Table 1

European's largest bioethanol producers [3–5]

Company	Country	Amount of installtions in Europe	Production milions of liters	Source
Abengoa Bioenergy	Spain	4	780	Wheat
Tereos	France	7	770	Wheat and beets
Crop Energies AG	Germany	3	760	Beets and sugar
Sudzucker	Germany	—	700	Wheat
Cristal Union	France	4	490	Sugar beets
Agrana Group	Austria	2	390	Wheat
Verbio	Germany	2	375	no data
Agroethanol AB	Sweden	1	210	Wheat
Industria Meridionale Alcolici (IMA)/Bertolino Group	Italy	1	200	no data
AlcoBioFuel	Belgium	1	150	no data
Prokon	Germany	1	120	no data
SEKAB (Svensk Etanolkemi)	Sweden	—	100*	Wood waste and excess wine

* – Data from 2006.

The largest company in Europe, which produces bioethanol, is Spanish Abengoa. Another large companies include: French confectionery Tereos and German: Crop Energies AG and Südzucker. An important place in the ranking is reserved for SEKAB, a Swedish company specializing in bio-ethanol production technology from lignocellulose, utilizing wood waste from paper industry (pulp), and excess of alcohol (wine). The guidance of the European Commission, which adjudicated on the possibility of managing the surplus of the product in the wine industry, encouraged company to use in the production wine stocks. SEKAB planned for 2008, invest in the production of bioethanol in Hungary. The plan was to build a four modern bioethanol plants for 380 million Euros, with a total production of 600 million liters (raw materials are mainly maize and wheat). By-product of this is over 460 000 tons of animal feed [3–5]. Unfortunately, market verified the plans. The increasing prices of raw materials (cereals) in combination with reduced harvest of corn in Hungary (compared to the expected), also possibility of changes in European Union standards (for biocomponent), effectively discouraged investors. The company projects SEKAB are suspended due to lack of funds and so far there's little possibility to change this situation. Hungary is now forced to cover their demand for bioethanol imports from Slovakia. SEKAB currently focused on promoting the new E-tech technology-based on bioethanol production from cellulose. The first stage of the raw material is subject to dilute acid (sulfuric acid or sulfur dioxide) and heat, which converts hemicellulose into sugar [6, 7]. Other part of the process are similar to any other processes of bioethanol production from lignocellulose.

The country, which strongly promotes the use of hydrated ethanol, is Brazil where pure ethanol is available at 26 thousand different fuel stations. The total number of cars, which are modified to use ethanol is more than 3 million. In recent years in the USA a significant increase in sales of E10 fuel has been observed – but still it is only 12 % of total sales of gasoline. The use of ethanol and its derivatives in both these countries is presented in Table 2.

Table 2

Amount of ethanol in a selected liquid fuels [1, 5]

Fuel	Country	Amount of ethanol
		% v/v.
Alcohol	Brazil	95.5
E85	USA	85
Gasoline	Brazil	24–26
Biodiesel	Sweden	15
E10	USA	10
Oxygenated fuel	USA	7.6
Reformulated gasoline	USA	5.7
BIO85	Poland	70–85

Ethanol and hydrogen are considered the most environmentally friendly fuels, because of lower emission during the combustion and the production process, when compared to other fuel production technologies, as well as because of the renewable raw materials used in production. The result is that in the analysis of the whole production cost, taking into account all stages of production, ethanol is classified as an environmentally friendly fuel.

Furthermore, analysis of total energy consumption in the production of bioethanol (including energy to produce fertilizers, agro-technical works, transportation of raw materials and products, and the processing of ethanol) indicate that the energy used to produce ethanol is lower than the energy obtained from its combustion, which causes a positive energetic and economical balance.

The characteristic of bioethanol

Bioethanol is defined as 99 % ethyl alcohol derived from biomass. In trade, as an alternative fuel, it can be used in pure form or as an additive to gasoline at different volume ratios. Table 3 contains the most important parameters to compare ethanol and gasoline. It is accepted that the name of bioethanol determining the percentage of ethanol in biofuel preceding them with the letter E (*eg* E 85). According to the European standard for diesel fuel (DIN EN 228), the ethanol concentration in gasoline may not exceed 5 % (E5). The use fuel with higher levels of ethanol in the vehicle inaccessible to the bioethanol may result in the loss of warranty. Bioethanol has a higher (by almost 10 units) octane number than gasoline, this can improve engine performance by increasing the degree of compression in the cylinder, however the use of pure fuel – 95 % ethanol – requires special engine construction. The standard also permits the use of other additives in the form of ethyl-t-butyl ether (ETBE – 47 % ethanol and 53 % of isobutene) in an amount not exceeding 15 %. ETBE has also a high octane number, and adding it to gasoline improves the resistance to explosive combustion. However, the raw material for the production of ETBE is also ethanol [8].

Table 3

Characteristic of bioethanol and comparison with gasoline [5, 8, 9]

Parameters		Ethanol	Gasoline
Energy equivalent	m^3	1.00	0.66
Heat of combustion	MJ/kg	29.3	43.5
Octane number	—	104	95
Annual yield (from corn)	m^3/ha	2.56	—
Increased consumption	%	25–30	—
Reduction of CO_2*	%	30–70**	—

* – Standard value in accordance with EU directives, ** – the fuel used in an industrial process.

Mechanism of alcoholic fermentation

One of the main methods of bioethanol production is a alcoholic fermentation, which is a hydrolytic decomposition of monosaccharides like: (glucose (honey), fructose (fruits), saccharose (beets, sugar cane)). Ethanol could be generated in a enzymatic decomposition of polysaccharides – starch (*eg* from corn and cereals) to monosaccharides in the hydrolysis process. Research is being conducted on a method of ethanol production from cellulose and hemicellulose from wood and straw. In this method, the raw materials is not food biomass but waste biomass and in future this production may become competitive to other technologies.

In the fermentation process, glucose is decomposed to alcohol and CO_2 by using yeast enzymes (zymase), according to the following reaction:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2 \qquad (1)$$

From a biochemical point of view, the alcoholic fermentation is a process of anaerobic sugar decomposition. This makes it possible for organism to thrive in anaerobic conditions (bacteria *eg* milk fermentation, cells of striated muscle in a effort, erythrocyte etc.). Alcoholic fermentation has three stages, one and two are similar like in milk fermentation – named glycolysis.

In the first stage, a glucose molecule, drived by ATP in the process of hexokinase, through gluco-6-phosphorane (glucose-fructose isomerase) is transformed with another ATP molecule into fructo-6-phosphorane which in turn causes the formation of 1,6-fructosediphosphate.

In the second stage, the diphosphat decomposes into 3-phosphogliceryne aldehyde or phosphodihydroxyacetone. These two compounds can be converted into each other by

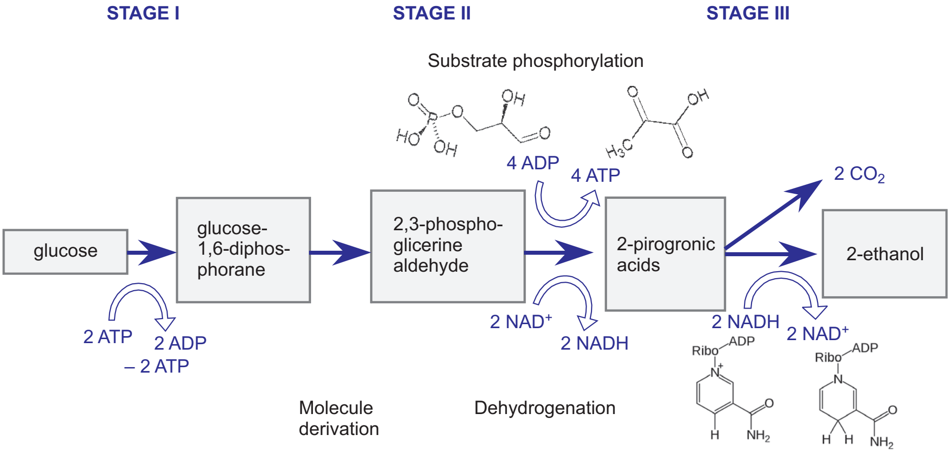

Fig. 1. The scheme presenting alcoholic fermentation process. ATP (*Adenosine Tri-Phosphate*), ADP (*Adenosine Di-Phosphate*), P_i (the rest of phosphoric acid), NAD (*Nicotinamide Adenine Dinucleotide*) and oxidized (NAD^+) and reduced form (NADH – *dehydrogenase*) [5, 10, 11]

mechanism of tri-phosphate isomerase. The two molecules of 3-phosphogliceryne aldehyde undergo transformations involving oxidation and phosphorylation, and the reactions are accompanied by the creation of four molecules of ATP and two molecules of pyruvic acid ($CH_3COCOOH$) [10, 11].

In the third stage, a decarboxylation of two molecules of pyruvic acid occures, through pyruvate decarboxylase. From two molecules of acetaldehyde (CH_3CHO) by alcoholic dehydrogenase with NAD, two molecules of ethyl alcohol are generated.

$$2CH_3COCOOH + 2H^+ \longrightarrow 2CH_3CHO + CO_2 \tag{2}$$

$$2CH_3CHO + 2NADH + 2H^+ \longrightarrow 2C_2H_5OH + 2NAD^+ \tag{3}$$

These three stages are shown in simplified terms, the graphic in Fig. 1, and their cumulative reactions is:

$$C_6H_{12}O_6 + 2ADP + 2P_i \longrightarrow 2C_2H_5OH + 2ATP + 2CO_2 \tag{4}$$

Bioethanol production technologies

Fermentation of ethanol is one of the oldest techniques of biotechnology. It uses micro-organisms, usually yeast: *Saccharomyces cerevisiae* capable of anaerobic conversion of monosaccharides to ethanol. The process of ethanol production can be divided into three main stages:

– preparation of raw material – enzymatic degradation of carbohydrate (starch, cellulose) into monosaccharides (glucose) by hydrolysis,

– ethanol fermentation – the processing of sugar conversion to alcohol, with emission of CO_2,

– separation of the product – distillation, ethanol dehydration and rectification [4].

Two different methods of preparation of raw material – wet or dry milling are used in ethanol production on an industrial scale. Before the fermentation process is carried out, the wet process requires the separation of raw material (separately on the germ, fiber, protein and starch). In modern distilleries, the grinding process of raw materials is carried out, followed by their enzymatic hydrolysis. In older agricultural distilleries, fermentation is carried out periodically, which in case of the new fermentation processes has been replaced by continuous extraction with ethanol or diffuse discharges. The use of vacuum extraction of fermentation products provides higher efficiency. These methods, due to their high cost and complexity, are not applied on an industrial scale yet.

The fermentation of broth is the primary microbial process. The yeast are need to carry out processes – these include: *Saccharomyces cerevisiae* and *Saccharomyces carlsbergensis* in the upper fermentation, or *Saccharomyces bayanus*, wine yeast, baking, and wild yeast (a mixture of many cultures) in case of lower fermentation.

Yeast used in brewing ferment at low temperatures 5–10 ^{o}C for about 1–2 weeks providing 2.5–5 % vol. alcohol. Optimum fermentation temperature is 25–30 ^{o}C and is used in distilling, where it takes 2–3 days, giving the mash content of 7–12 % alcohol, but also a large amount of pollutants. Pollutants are disposed of by refining, rectification and using activated carbon adsorption. The turbulent and secondary fermentation of wine is carried out at lower room temperature, and therefore takes longer: 1–2 months (maturing for several years), but the resulting product has only trace amounts of fusion, giving it a special flavor and taste, specific for the vineyard.

Ethyl alcohol is separated from the fermentation residues using the distillation, and the boiling temperature difference using the two others components (ethanol boils at 78.3 ^{o}C). Unfortunately, ethanol and water form an azeotrope mixture, which has a boiling point of 95.6 % ethyl alcohol, about 4 % water and the rest (higher alcohols, esters, ethers and acids). Even a small amount of water is unacceptable, because it can cause the presence of water in the fuel mixture. Therefore, only anhydrous alcohol (99.5–99.9 %) should be used as a fuel.

Figure 2 shows an example diagram of ethanol production in grain distillery.

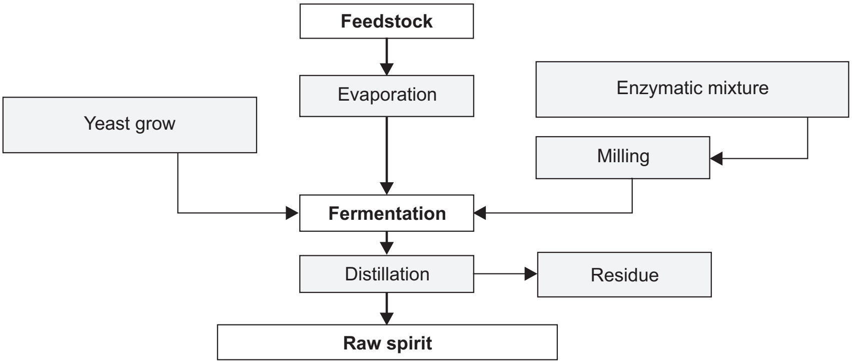

Fig. 2. The scheme of alcohol production in grain distillery [5]

The agricultural distilleries are used as distillation columns, designed for continuous work, the shelves separate raw spirit of broth digestate.

In distilleries, a 95.6 % mixture of ethanol and water is produced, commonly known as spirit. It is in fact an azeotropic mixture and the pure ethanol couldn't be generated from it. In order to obtain the pure ethanol (100 %), azeotropic distillation is conducted in the ethanol-water-benzene system. After adding a small amount of benzene, initially there is a threefold process of boiling azeotrope benzene-ethanol-water, then ethanol--benzene azeotrope, and finally the process of distilling to pure anhydrous ethanol. It is possible to bound water with 95.6 % ethanol by adding calcium oxide or anhydrous magnesium sulphate (VI) or sodium sulphate (VI). Absolute ethanol is hygroscopic and absorbs water from the air, so it should be stored it in hermetic containers. Completely anhydrous ethanol (water content < 100 ppm) is obtained by distillation from over magnesium ethoxide in the system protected from air [12, 13].

The distillery produces low wine, containing about 90–92 % ethanol. It is processed in rectification plants to the anhydrous or consumption alcohol. To obtain anhydrous alcohol, molecular sieves are (sorption of water in a suitable sorbent) [1].

Iogen technology

Bioethanol production technology proposed by Iogen company is based on a combination of thermal, biomass chemical and biochemical conversion into a fuel called cellulosic ethanol [14–16]. Cellulosic ethanol is produced in an amount of more than 340 liters per ton of fiber.

Lignin, present in plant's fibers is processed and used as fuel for process steam and electricity. This eliminated the need of additional coal or natural gas, and also reduced CO_2 emissions. In the process of pre-treatment, which is to increase the surface and "availability" of plant fibers to the enzymes, special water vapor injection systems are utilized. It improves the performance of both the pre-treatment and ethanol production, which provide lower cost of the fuel. The company has also developed its own cellulose enzyme groups and delivers them worldwide to pulp, paper, textiles and animal feed industries. Diagram of the production of bioethanol by Iogen is shown in Fig 3.

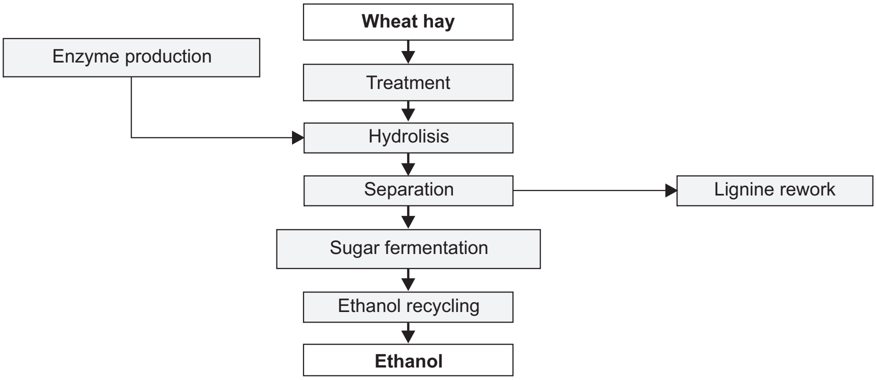

Fig. 3. The scheme of ethanol production by Iogen technology [5, 17]

Iogen's demonstration plant has been producing cellulosic ethanol from wheat straw since 2004. At full capacity it process 20–30 t/day of feedstock and produce approximately 5000–6000 l/day of cellulosic ethanol. In 2009, Iogen became the first cellulosic ethanol producer to sell its advanced biofuel at a retail service station. For a one month period, a 10 % cellulosic ethanol blend was available for sale to the general consumers. More than 2 mln. litres of Iogen's cellulosic ethanol has been produced until 2012.

ICM technology

Technology adopted by ICM uses dry milling process in which grain is grinded for sharps. The starch contained in it is easier and faster converted into ethanol by fermentation process. Technology proposed by the ICM is presented in Fig. 4 [18].

Silos for the storage of grain are sufficient to supply the production line for 7–10 days. From the tray material goes to the hammer mills, preceded by a set of screens

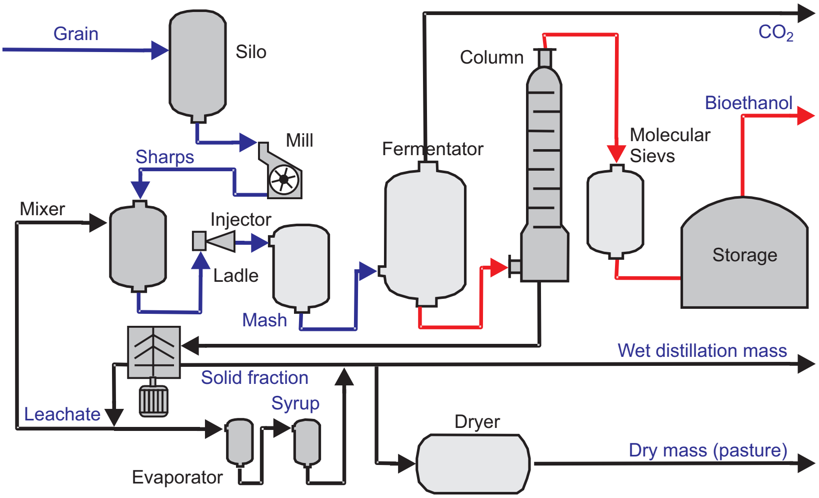

Fig. 4. The scheme of ethanol production by ICM technology [5, 18]

designed to remove residual stems, stones and ground, which could hinder the process of grinding. The ground grains are mixed with: process water (with pH of about 5.8) and enzyme (α-amylase). The slurry is then heated to a temperature of 82–88 ^{o}C for 30–45 minutes to reduce its viscosity and pumped pressurized steam injector, which also heats the mash to the 105 ^{o}C. After 5 minutes, the mash is cooled in the tank with air at reduced pressure to a temperature of 82–88 ^{o}C and left for 1–2 hours to make sugar from starch into short concatenation dextrin.

After the initial stage of saccharification and addition of a second enzyme – glucoamylase, the mash is pumped into fermentation tanks.

In the glucoamylase fermentation process, dextrin is broken down into simple sugars, then yeast is added, which provides the conversion of sugar into ethanol and carbon dioxide. The mash is allowed to ferment for 50–60 hours, resulting in the final mixture containing about 15 % ethanol, also solid residues from grain and yeast. The fermented mash is pumped into the distillation columns, which provides additional warmth. Product leaving the distillation columns contains about 95 % (by volume) ethanol. The residue from this process (containing raw materials and water) is pumped from the bottom of the column to the centrifuges.

The resulting ethanol, containing still 5 % of water, is directed to a molecular sieve to physically separate the water and ethanol, based on the difference in particle size between those substances. After going through this stage anhydrous ethanol is obtained. Small amounts of denatured alcohol are added before storage tanks. This contamination prevents distribution and use of this alcohol as a consumer product. Most of the tanks in the factory of ethanol are so capacious that they allows the storage of the product (as in the case of material) for 7–10 days.

The process of fermentative production of ethanol creates two by-products: carbon dioxide and stillage (cereal, potato). CO_2 can be captured and treated in a scrubber, and then launched to sold of agri-food processing, *eg* for aerating beverages. While the stock is headed to the centrifuges, where is separated into two fractions: a rare (liquid containing 5–10 % solids) and a thick *wet solid residue* (WDG). Some of thin stillage is recycled to the process, which reducing the demand of process water. The rest is directed to a system of evaporators, where it is concentrated to a syrup having a concentration about 25–50 %. This syrup, high in protein, yeast, sugar and fat, is used to enrich WDG. This could be perfect fodder for farm animals. Many bioethanol plants aren't near the farmers to take advantage of all the WDG produced. Long term storage of such products is not a solution, because of the short life span of wet stillage (because of rapid biodegradation). In this case, the additional drying system is used, which removes moisture and prolongs its life span. Dry stillage (DDG) is used as high-protein feed ingredient of cattle, pigs, poultry and fish.

In 2012 ICM, Inc. also announces that it successfully completed 1,000-hour run of its pilot plant based on Integrated Fiber to Cellulosic Ethanol Technology, designed for the production of cellulosic ethanol at existing grain ethanol plants. Company has proved substantial operating and capital expense cost savings over a traditional approach of cellulosic ethanol production [19, 20].

Technology using supercritical water

A new, exciting technology for the production of bioethanol is developed at Kyoto University [21]. Lignocellulose in biomass is subjected to the water in the supercritical state (T > 374 ^{o}C, p > 22.1 MPa). The hydrothermal reaction of oxidative reforming, forming the fraction soluble in water and methanol, other soluble fraction only in methanol and lastly an insoluble residue. Hydrolysis products of carbohydrate derivatives, dehydrated, and shredded products and organic acids are the water-soluble substances. The residue is a mixture of glucan (polysaccharide) and lignin, which are

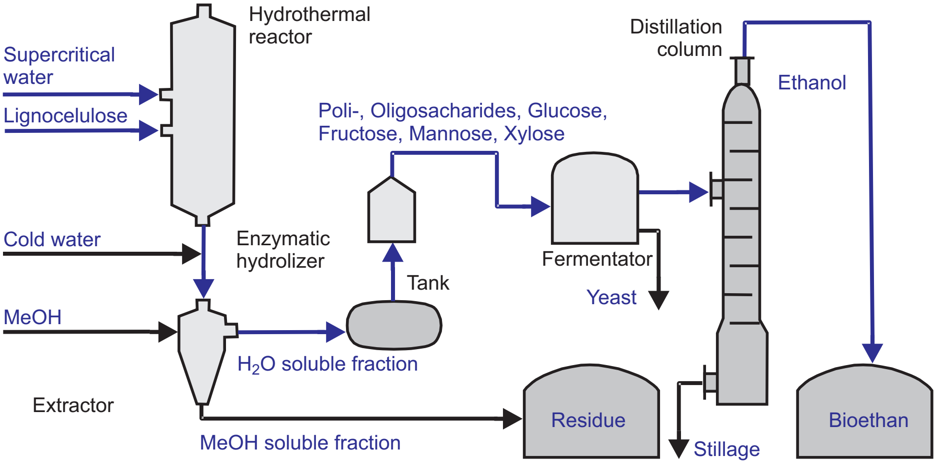

Fig. 5. The scheme of ethanol production and lignin derivative [21, 25]

insoluble in water, but are soluble in supercritical water, soluble in methanol part is derived from lignin.

The use of supercritical water allows the pre-treatment of lignocellulose, involving the rupture of her long, chemically stable, chains for simple sugars, which are already subject to fermentation in the traditional production of ethanol. The course of this technology is shown in Figure 5.

The biomass resilient to ethanol fermentation (wood, straw, Lety, cake, etc.), that contains lignocellulose is transported into reactor for hydrothermal decomposition with supercritical water. Products of hydrothermal decomposition, after the cold water addition, are pumped to the extractor, where the separation of water-soluble products from the methanol-soluble products occurs.

The first of these fractions, containing products of cellulose and hemicellulose decomposition, is subjected to saccharification processes in an enzyme hydrolyser, then after the fermentation, distillation and rectification is generating the product which is bioethanol.

The remaining, soluble in methanol, fraction containing aromatic compounds, derived from hydrothermal decomposition of lignin, is converted into other useful products (solvents, intermediates and chemical reagents). A team of researchers from Kyoto is still conducting research to optimize this technology [5, 22, 23].

Usefulness of water in the under or supercritical state as a solvent, reagent and catalyst of acid / alkaline in recent years is the subject of intensive research, which tends to use it in: chemical synthesis reactions, conversion processes, gasification, biomass processing, and wastewater treatment [24].

Biorafineries as a perspective for development of bioethanol

Main research aiming at improving efficiency of bioethanol production is conducted in the following areas: raw material acquisition in form of waste or biomass, which does not undergo alcoholic fermentation, developing methods for pretreatment of biomass, the use of carbon dioxide and ammonia for decomposition of biomass and synthesis of more efficient enzymes.

In these studies, special emphasis was placed on the acquisition and use of more diverse material in the production of bioethanol, for example, waste from wood, crop residues, firewood from the forests, plants and municipal waste. The chemical structure of this potential raw material is much more diverse than traditional distilling material to which ethanol is the main source of starch or sugar. However, this requires solving many technological and chemical processes.

Due to the high costs of such an enterprise the Swiss company Syngent, has signed a 10-year contract worth 16 million with USA company Divers for research and development of bio-ethanol production technology, the complexity of which is a diagram included in Fig. 6 [3]. Industrial start of the following technology is estimated for next 8–12 years.

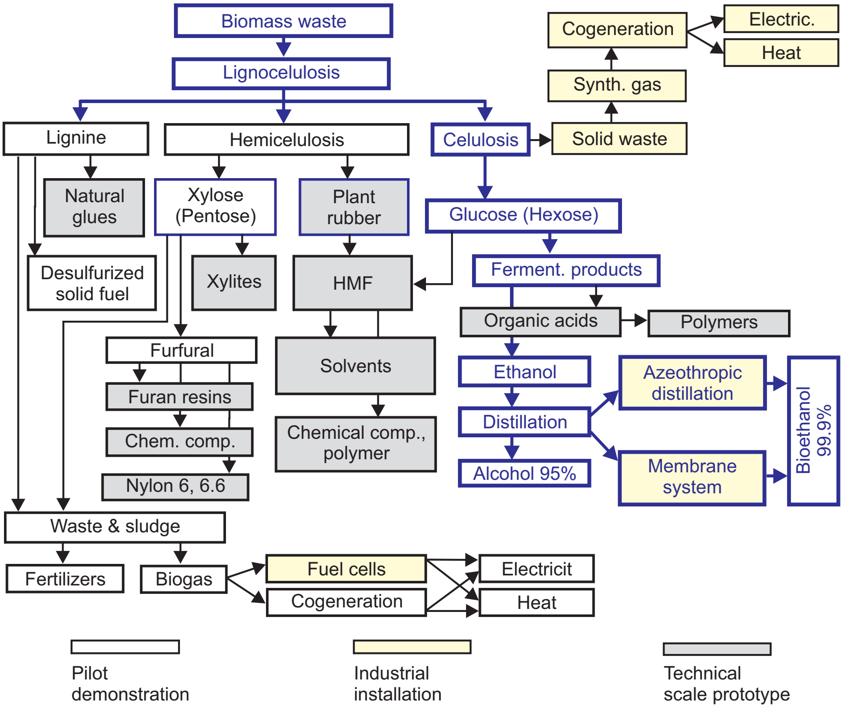

Fig. 6. The scheme of biorafineris conception. [3, 4, 25]

Bioethanol in Poland

Bioethanol production in Poland remains at the same level for several years. Its average annual value exceeds 122 000 tons. Bioethanol production in Poland has been increased by less than 80 % from the year 2005 to 2012 and by almost 20 % in the last year. Nearly one million tons of bioethanol was produced in Poland in this period, which accounted 32 % of the total domestic production of biofuels and biocomponents. Unfortunately, there are only few times we can talk about the supplies over demands surplus, which shows the potential in bioethanol production for export purpose.

By decree of the Minister of Economy (Journal of Laws 2010 No. 122, item. 830) bioethanol fuel is marked in Poland as BIO85. This is a new biofuel containing from 70 % to 85 % (vol.) of bioethanol and 15–30 % of gasoline in the mixture. The composition of the mixture depends on the seasons: summer, interlude or winter. The quality of BIO85 biofuel was determined by the Regulation of 22 January 2009 on quality requirements for liquid biofuels (Journal of Laws No. 18, item. 98). PKN ORLEN SA was the first company which introduced BIO85 biofuel into retail sale in Poland. Representatives of Ford and Volvo have signed letters of intent with the Company for joint cooperation in the area of promoting BIO85. So far it can be bought at one station in Warsaw. The openings of the stations in other cities are subjected to the success of the pilot program in Warsaw and increase of the market share of vehicles with engines adapted for this fuel in Poland. Therefore, at the end of 2013 the BIO85 biofuel is still not available at other petrol stations of PKN ORLEN SA.

Previously listed technologies, especially the ICM, can be easily transferred to Polish conditions. Especially now, when the demand for alcohol is not sufficient to maintain many companies, producing ethanol. However, without the support of the international companies the use of these technologies in Poland seems to have little chance for success.

Summary

In this study, a collection of examples of modern technologies allows obtaining ethanol has been presented. It systemizes knowledge in the field of liquid biofuels, based on the alcoholic fermentation. Proposed future solution, in the form of biorefineries is setting new trends and gives hope for further development and implementation of research in this area over the next decade.

With the continuation in the current growth rate of the biofuels production, which annually is 7.0 % in Europe, 2.5 % in North America and Brazil and 2.3 % globally, in 2020 the world production of biofuels should reach a value of more than $4 \cdot 10^7$ m^3. However, as a result of the campaign promoting biofuels, their production growth rate, rather than linear, may take exponential character and then, according to one of the scenarios, the annual production of biofuels in 2020 could reach $1.2 \cdot 10^8$ m^3 [26].

European countries are now at the forefront in the production of biodiesel based on rapeseed. However, current global production of biodiesel is about 16 times less than the bio-gasoline (about $1.75 \cdot 10^6$ m^3/a in 2004) [26]. Therefore, the global leaders in the production of biofuels are (and probably will remain for a long time) Brazil and the United States.

Implementation of described in this paper bioethanol technologies in the polish conditions, can bring tangible benefits for local companies. Although these technologies are still evolving, and it is difficult to talk about specific efficiencies, it is certain that bioethanol production and export could provide viable alternatives for polish ethanol plants, which have problems with the disposal, or have plans to expand their production portfolio.

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METODY PRODUKCJI BIOPALIW CIEKŁYCH NA PRZYKŁADZIE BIOETANOLU

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Abstrakt: Etanol, poza wykorzystaniem w przemyśle spożywczym oraz chemicznym, gdzie służy jako rozpuszczalnik i substrat syntezowy, w ostatnich czasach zyskał równie ważne zastosowanie w branży paliwowej. Produkowany jest na skalę przemysłową, głównie z substratów nienadających się do spożycia i występuje pod zwyczajową nazwą bioetanol, pełniąc funkcję biopaliwa lub dodawanego do benzyny w różnych proporcjach biokomponentu. Z uwagi na stosunkowo prosty sposób produkcji, wykorzystujący mechanizm fermentacji, znanych jest dziś kilka technologii produkcji bioetanolu, a zainteresowanie ich wykorzystywaniem i ulepszaniem jest wciąż znaczne. Biorąc pod uwagę rosnące zapotrzebowanie na paliwa alternatywne, bioetanol jest dziś jednym z najbardziej nośnych tematów badawczych i wdrożeniowych w sektorze paliwowym. Niniejsza praca stanowi podsumowanie dotychczasowej wiedzy w tym temacie. Przytoczono w niej dane, dotyczące największych producentów etanolu i bioetanolu na świecie oraz analizę wykorzystania tego biopaliwa w poszczególnych krajach. Wskazano charakterystykę samego bioetanolu, mechanizm jego produkcji i schematycznie przedstawiono najważniejsze technologie produkcji. Praca zawiera również opis najbardziej prawdopodobnego przyszłego wykorzystania biopaliw – budowę biorafinerii nowej generacji.

Słowa kluczowe: biopaliwa, bioetanol, technologie produkcji

Varia

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