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Monika BOJANOWSKA[1] and Jerzy TYS[2]

DETERMINATION OF THE LEVEL OF B[a]P CONTENT IN RAPE SEEDS SUBJECTED TO VARIOUS POST-HARVEST TREATMENTS

OKREŚLENIE POZIOMU ZAWARTOŚCI B[a]P W NASIONACH RZEPAKU PODDANYCH ZRÓŻNICOWANEJ OBRÓBCE POZBIOROWEJ

Abstract: Polycyclic aromatic hydrocarbons (PAH) constitute one of the largest and most varied groups of organic compounds with known toxic, mutagenic and carcinogenic properties characteristic of many representatives of the group. Food contamination with PAH may result not only from environmental pollution but also from certain technological processes used in processing of raw materials and in storage of agricultural food products. The objective of the presented study was to determine the benzo[a]pyrene content in rape seeds subjected to various post-harvest treatments and processing.

The study showed that rape seed contamination with B[a]P is dependent primarily on the temperature of drying, but also on the regions of cultivation and on the weather conditions in particular years.

Keywords: benzo[a]pyrene, rape seeds

The occurrence of polycyclic aromatic hydrocarbons in agricultural food products is caused by their common presence in the environment and penetration into plants during their vegetation or as a result of technological processes of food preservation [1]. In recent years, in numerous countries, requirements have been published concerning the content of PAH in vegetable fats. And thus, in Germany it is recommended that the content of total PAH should not exceed 25 $\mu g \cdot kg^{-1}$, according to the British requirements the content of benzo[a]pyrene (B[a]P) should not exceed 2 $\mu g \cdot kg^{-1}$, and acc. to the Spanish ones – 5 $\mu g \cdot kg^{-1}$ [2]. Observed in Poland level of contamination of agricultural materials (rapeseed, among other things) and food products with polycyclic aromatic hydrocarbons does not differ from that observed in other countries (and accepted by the requirements of the world standards). The highest share in the uptake of

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[1] Department of Chemistry, University of Life Sciences in Lublin, ul. Akademicka 15, 20–950 Lublin, Poland, phone 81 445 6640, email: monika.bojanowska@up.lublin.pl

[2] Institute of Agrophysics Polish Academy of Sciences, ul. Doświadczalna 4, 20–290 Lublin, Poland, phone 81 744 5061, email: jtys@demeter.ipan.lublin.pl

PAH is that of agricultural products, and especially products of plant origin, which PAH content is low, but the level of their consumption is very high [3, 4].

The degree of rapeseed contamination with PAH depends on the region of cultivation, level of contamination of the environment, and contamination resulting from drying and supplementary drying of seeds. Frequently, rape seed is dried using dryers that do not meet technical and operational requirements, eg such in which air circulation is forced without the use of heat exchangers or with damaged exchangers, and additionally without control of quality of the drying medium [5].

Monitoring of threats related with the occurrence of PAH appears to be strongly recommended due to the presence of B[a]P in samples that were not subjected to the processes of postharvest treatment. This indicates the common occurrence of the compound in the human environment [6].

The objective of the presented study was determination of the content of benzo[a]pyrene in rape seeds subjected to various post-harvest treatments.

Material and methods

The material for the study consisted of samples of rape seed obtained from suppliers of the raw material from the regions of the north, south and west of Poland.

Determinations of benzo[a]pyrene were made with a method based on high-efficiency liquid column chromatography (HPLC) using an US-made Waters liquid chromatograph equipped with Controller 600, Waters 600E Multisolvent Delivery System pump and Waters 996 Photodiode Array Detector with resolution of 1.2 nm. Operation of the chromatograph and data acquisition and processing were made with the use of the Millennium Version 3.05 software package.

The studied solutions, obtained after ultrasonic extraction of benzo[a]pyrene from rape seed samples by means of acetonitrile, were concentrated, purified and extracted using the “BAKER spe 12G” system with spe filtration columns with two 20 μm PE sinters and 0.45 μm filters and with Oktyl C_8, 500 mg separation columns, and then sprayed onto a Nova-Pak®, C18, 60 Å, 4 μm, 3.9×150 mm column. Deaeration (deoxygenation) of eluents was conducted with the use of helium at the rate of 30 $cm^3 \cdot min^{-1}$.

Remaining conditions of chromatographic analysis were: elution: gradient – 95 % acetonitrile – 5 % water, mobile phase flow rate: 1 $cm^3 \cdot min^{-1}$, injection: 20 mm^3, wavelength: $\lambda = 254$ nm, limit pressure above which flow stops: 3600 PSI, measurement temperature: 25 °C. Recovery, limit of detection and coefficient of variation for determinations of benzo[a]pyrene were 91.23 %, 0.12 $\mu g \cdot kg^{-1}$ and 4.26 %, respectively.

Reagents used for the analyses were BAKER ANALYZED® HPLC-reagent, while the standards were prepared from benzo[a]pyrene produced by Fluka.

Results and discussion

The obtained results describing the content of benzo[a]pyrene indicate that the compound occurs in greater amounts in samples of seeds subjected to the process of drying. This demonstrates that the treatment is the most hazardous in the process of postharvest processing.

Drying temperature proved to be a factor significantly affecting the content of B[a]P in rape seeds (Fig. 1).

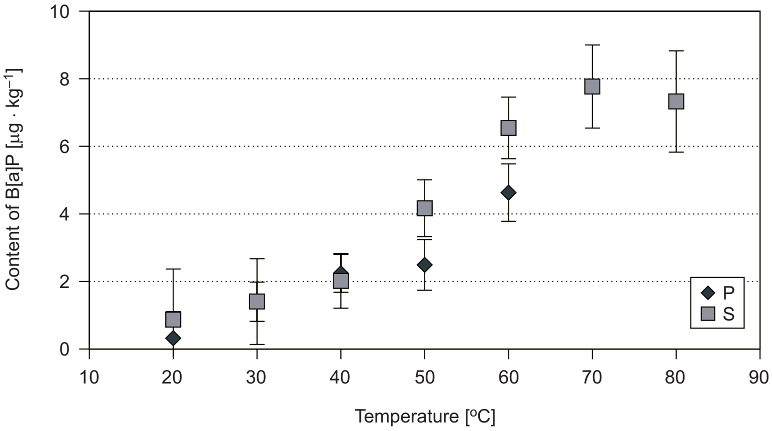

Fig. 1. Effect of drying temperature on the content of benzo[a]pyrene in rape seeds: S – dried seeds, P – seeds before drying

Within the temperature range of 20–40 °C there occurred the lowest level of contamination with B[a]P, at the level from 0.32 to 2.24 µg · kg^{-1}, both for samples subjected to the process of drying and for those immediately after the harvest. For the drying temperature of 50 °C, the content of benzo[a]pyrene increased two-fold, and at temperatures of 60 °C and 70 °C increase by 70 and 75 % in the level of B[a]P, respectively, was recorded, which clearly demonstrates the growing hazard of seed contamination with increase in the temperature of drying. A slight decrease in the content of benzo[a]pyrene at the temperature of 80 °C may be attributed to partial decomposition of the compound at high temperature, which is supported by data available [7, 8]. Decreasing content of benzo[a]pyrene in rape seeds subjected to the effect of high temperature creates the risk of their contamination with the products of its decomposition that often prove to be more toxic due to the better solubility of lighter PAH in water [9].

In rape seed delivered to oil producing companies in the regions of southern and western Poland, in a great majority of samples the values did not exceed the level of 2 µg · kg^{-1} (Fig. 2).

The lack of very high amounts of B[a]P (individual cases at the level of 3–4 µg · kg^{-1}) and the use of relatively low drying temperatures (mostly within the range of up to 50–60 °C) indicate very good condition of drying plants in those regions and observance of principles of safe food production by the producers. In isolated cases a relatively high content of benzo[a]pyrene was observed in spite of the use of low drying

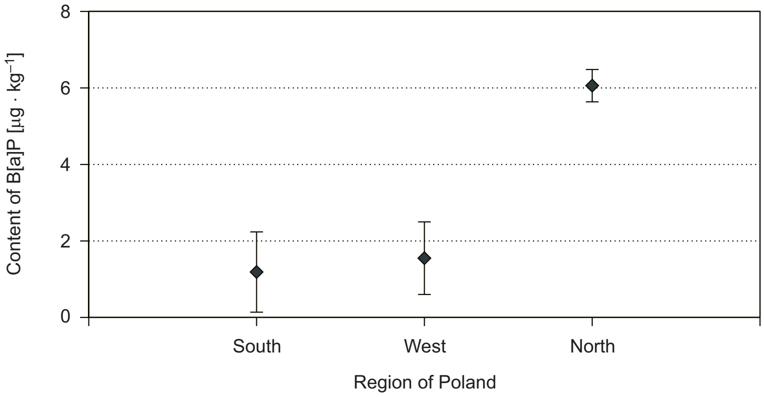

Fig. 2. Effect of region of cultivation on the content of benzo[a]pyrene in rape seeds

temperature (30–40 ^{o}C). This may be a result of drying rape seed with air without heat exchangers (a measure applied by unreliable producers for reasons of economy).

Results of analysis of samples obtained in the particular years of the study indicate that also different weather conditions may cause variation in that feature of seeds, so important for health (Fig. 3).

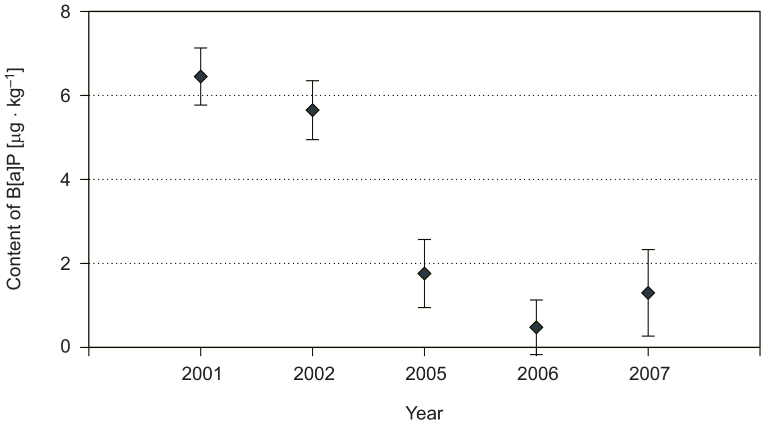

Fig. 3. Effect of year of cultivation on the content of benzo[a]pyrene in rape seeds

Worse weather conditions during harvest in 2001 had an effect on the conditions of rape seed drying (samples with high moisture content required longer drying). Seeds produced under such conditions displayed notably higher level of contamination with B[a]P compared with seeds from 2002 which was a year with much more favourable weather conditions. Another cause of contamination is the age and technical condition of dryers used by rape seed producers.

Most of the samples tested in 2001–2002 came from producers from the north of Poland. A study by Rybacki et al [10] showed that more than a half of the dryers in use in that region are older than 15 years, and 24 % of them were made before the year 1980. Most of the dryers are operated after considerable modifications and upgrades that not always resulted in sealing of the heating elements that would preclude exhaust fumes penetration to the material dried. For these reasons, the highest amounts of benzo[a]pyrene were recorded in the region of suppliers from the north of Poland. The year 2006 was characterised by high temperature and low amount of rainfall during the vegetation and harvest of rapeseed, hence the lowest level of B[a]P in the seed that mostly did not require supplementary drying. In 2007, on the other hand, in spite of not really favourable weather conditions, relatively low levels of benzo[a]pyrene were found in the seed, which may have been a result of increased awareness of the producers with respect to food safety and observance of regimes in the process of rape seed drying. Lower content of that compound in seeds obtained in the years 2005–2007 was also due to the activity of agricultural services that eliminate from the list of suppliers those producers who provide seed that is the worst in this respect.

Rapeseed is one of the major crop plants grown in Poland for many years, and is the fundamental raw material for the production of vegetable oil. The results of the presented study show that rape seed contamination with benzo[a]pyrene is at a level acceptable in terms of the relevant world standards. However, the occurrence of individual samples of dried seed in which the content of B[a]P exceeds the level of 8 $\mu g \cdot kg^{-1}$ (from the region of northern Poland) indicates that the problem of rape seed contamination with PAH exists, and control of raw material for oil production is a necessity. In some European countries (Czech Republic, Germany) actions are undertaken to reduce the level of benzo[a]pyrene when food product contamination occurs at the level of 2 $\mu g \cdot kg^{-1}$ [11, 12]. Also significant is the fact that rape seeds are only the raw material that is then subjected to complex processes of refinement and purification, in the course of which a notable part of noxious compounds can be removed.

Conclusions

1. Generally, the content of benzo[a]pyrene in rape seeds does not exceed the standards in force in the EU countries.
2. The process of rape seed drying is one of the major sources of contamination with B[a]P. This creates the necessity of continuous control of dryers, aimed at elimination of unreliable producers from the approved list of suppliers of the material.
3. Temperature of drying is the most important factor determining the content of benzo[a]pyrene in rape seeds. Firstly, application of high temperature increases the level of the compound, and secondly – the products of its decomposition may cause a decrease in the health value of the seeds.

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OKREŚLENIE POZIOMU ZAWARTOŚCI B[a]P W NASIONACH RZEPAKU PODDANYCH ZRÓŻNICOWANEJ OBRÓBCE POZBIOROWEJ

[1] Katedra Chemii, Uniwersytet Przyrodniczy w Lublinie
[2] Instytut Agrofizyki PAN w Lublinie

Abstrakt: Wielopierścieniowe węglowodory aromatyczne (WWA, PAH) stanowią jedną z największych i zróżnicowanych grup związków organicznych o znanych właściwościach toksycznych, mutagennych i kancerogennych, którymi cechuje się wielu przedstawicieli tej grupy. Skażenie żywności nimi jest wynikiem nie tylko skażenia środowiska, ale może być również rezultatem niektórych procesów technologicznych stosowanych w przetwórstwie surowców i przechowalnictwie produktów rolno-spożywczych. Celem podjętych badań było określenie poziomu zawartości benzo[a]pirenu w nasionach rzepaku poddanych zróżnicowanej obróbce pozbiorowej. Przeprowadzone badania wykazały, że zanieczyszczenie nasion rzepaku B[a]P jest uzależnione przede wszystkim od temperatury suszenia, ale także rejonu uprawy, jak również od przebiegu pogody w poszczególnych latach.

Słowa kluczowe: benzo[a]piren, nasiona rzepaku

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Teresa BOWSZYS[1], Jadwiga WIERZBOWSKA[1],
Justyna BOWSZYS[1] and Arkadiusz BIENIEK[2]

CONTENT OF SOLUBLE LEAD AND CADMIUM FORMS IN SOIL FERTILIZED WITH SEWAGE SLUDGE COMPOSTS

ZAWARTOŚĆ ROZPUSZCZALNYCH FORM OŁOWIU I KADMU W GLEBIE NAWOŻONEJ KOMPOSTAMI Z OSADÓW ŚCIEKOWYCH

Abstract: In 2004–2007, an experiment was conducted at the Production and Experimental Station in Balcyny near Ostroda. The experiment was established on proper podsolic soil formed from light clay loam, which was rich in available P, moderately abundant in K and poor in Mg. The experiment comprised a 4-field crop rotation system (potato, spring barley, oilseed rape and winter wheat). It was designed according to the random block method and consisted of 8 objects (2 series, 4 objects each): 1. FYM, 2. composted municipal sewage sludge with straw (from Ilawa), 3. Dried and granulated sewage sludge (from Ilawa), 4. Composted sewage sludge (from Ostroda). In series 1 the composts and manure were used in single doses (in 2004) at a rate of 10 Mg d.m. · ha^{-1}, and in the following years mineral fertilization alone was applied. In series 2 the same organic fertilizers were split into two doses: 5 Mg d.m. · ha^{-1} each (to soil cropped with potato and winter oilseed rape). In all the objects amended with organic fertilizers and farmyard manure, depending on the total nitrogen content, nitrogen was balanced to the amount of 150 kg · ha^{-1} in 2004 and 120 kg · ha^{-1} in 2005. Spring barley and winter wheat received only mineral fertilization.

A small increase in the content of Pb and Cd was observed over the four years of the experiment in the soil fertilized with the sewage sludge composts versus soil amended with FYM. Analysis of soil after crop harvest showed that the content of the test heavy metals did not exceed the values considered to be the natural ones. For lead, these values ranged on average between 8.9 to 11.2 mg · kg^{-1} and for cadmium – between 0.10 to 0.22 mg · kg^{-1}.

Keywords: sewage sludge, soil, lead, cadmium

Sewage is a valuable source of organic and mineral substances. High content of organic matter in sewage composts has an advantageous effect on physicochemical and buffer properties of soils and, in addition, improves water and air relationships within soil profiles [1, 2]. Sewage also contains macro- and microelements which are essential

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[1] Department of Agricultural Chemistry and Environment Protection, University of Warmia and Mazury in Olsztyn, ul. M. Oczapowskiego 8, 10–744 Olsztyn, Poland, phone 89 523 3239, email:bowter@uwm.edu.pl

[2] Department of Soil Science and Soil Protection.

plant nutrients, stimulating many biochemical processes that occur in plant tissues [2–5]. In Poland, sewage is most often deposited close to its point of origin, whereas in many other EU countries it is utilized in agriculture or forestry. The value of composts produced from sewage sludge is impaired mainly by the heavy metals found in it [6–8]. Heavy metals are very toxic to living organisms, therefore they create a serious problem when trying to utilise certain biowaste. The following heavy metals are considered to be capable of making hard reversible damage in ecosystems: cadmium, mercury, lead, zinc, copper, nickel and chromium.

The objective of our study has been to determine the immediate and subsequent effects of municipal sewage sludge as well as sewage sludge composts on the content of mobile forms of lead and cadmium in soil.

Material and methods

In 2004–2007, a field trial was conducted at the Production and Experimental Station in Balcyny near Ostroda, Poland. The experiment was established on proper podsolic soil formed from light clay loam, which was rich in available P, moderately abundant in K and poor in Mg. A 4-field crop rotation system (potato, spring barley, winter oilseed rape, winter wheat) was introduced. The experiment, which was established using the random blocks design method, consisted of 8 objects (2 series, 4 objects each): 1. FYM, 2. municipal sewage sludge composted with straw (from Ilawa), 3. dried and granulated sewage sludge (from Iława), 4. composted sewage sludge (from Ostoda). In series 1, composts and manure were applied singly (in 2004) at a rate of 10 Mg d.m. · ha^{-1}, followed exclusively by mineral fertilization in the other years. In series 2 the same fertilizers were introduced at a rate of 5 Mg d.m. · ha^{-1} to soil cropped with potato and 5 Mg d.m. · ha^{-1} to soil under winter oilseed rape. In the soil objects treated with organic fertilizers and manure, depending on their total N content, nitrogen was balanced to 150 kg · ha^{-1} in 2004 and to 120 kg · ha^{-1} in 2005. Spring barley and winter wheat were fertilized with mineral fertilizers alone.

Prior to the experiment, soil, manure and compost samples were collected for analysis. The samples were averaged, after which the following determinations were made: pH in 1 mol KCl · dm^{-3} (5.04), Pb and Cd content extracted with 1 mol HCl · dm^{-3} by the AAS method, using an AA-6800 Shimadzu spectrophotometer (Table 1). The results were compared with the certified material (Table 2).

Table 1

Content of Pb and Cd in soil, FYM and composts before the experiment [mg · kg^{-1} d.m.]

Metal	Soil	FYM	Sewage sludge		
			composted	with straw	dried and granulated
Pb	9.90	8.40	12.41	11.46	16.54
Cd	0.13	0.31	4.58	1.42	11.08

Table 2

Determinations for the certified material

Value [mg · kg^{-1}d.m.]	Virginia Tobacco Leaves CTA-VTL-2	
	Cd	Pb
Certified	1.52 ± 0.34	22.1 ± 1.2
Determined	1.68 ± 0.41	23.2 ± 1.3

The results of the experiment (from each plot) underwent analysis of variance, with the significance of differences determined at the level of significance $\alpha = 0.05$.

Results and discussion

Municipal sewage sludge composts are most often neutral or alkaline in reaction, and can be used to neutralise acidic soils [2, 6]. The composts tested in presented study caused an increase in the soils' pH value (Table 3).

Table 3

Soil reaction after harvest [1 mol KCl · dm^{-3}]

Year	Application method	FYM	Sewage sludge		
			composted	composted	composted
2004	a	5.27	5.45	5.36	5.39
	b	5.06	5.37	5.11	5.37
2005	a	4.95	5.10	5.02	5.09
	b	4.90	5.06	4.95	5.03
2006	a	5.02	5.21	5.18	5.27
	b	5.03	5.21	5.09	5.21
2007	a	5.27	5.18	5.22	5.20
	b	5.11	5.46	5.25	5.46

Explanations for Table and Figures: a – single dose of 10 Mg d.m. · ha^{-1} applied once in the crop rotation system, b – two applications, 5 Mg d.m. · ha^{-1} each, applied in the crop rotation system.

The immediate and subsequent effect of the test fertilizers on the value of soil pH were superior when a single rate of a fertilizer (10 Mg d.m. · ha^{-1}) was applied. However, in 2005 the soil reaction was noticed to be approximately identical to the original one. Likewise, Szulc et al [8] found out that fertilization with composts improves acidification indices (pH, Hh). Similar relationships were reported by Weber et al [9]. After harvesting winter oilseed rape, which had received the second dose of FYM or composts (series 2), all the objects were similar in soil reaction. The subsequent effect of the second dose of the biowaste on soil reaction was stronger than in the previous year.

The results of the study suggest that the content of mobile lead and cadmium forms in soil was significantly affected by the type of fertilization regime (Figs. 1 and 2).

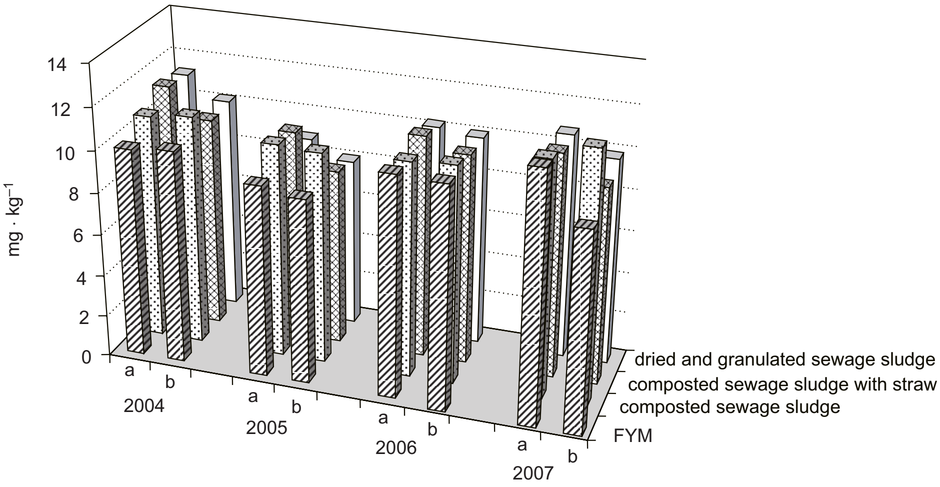

Fig. 1. Content of Pb in soil after harvest; explanations as under Table 1

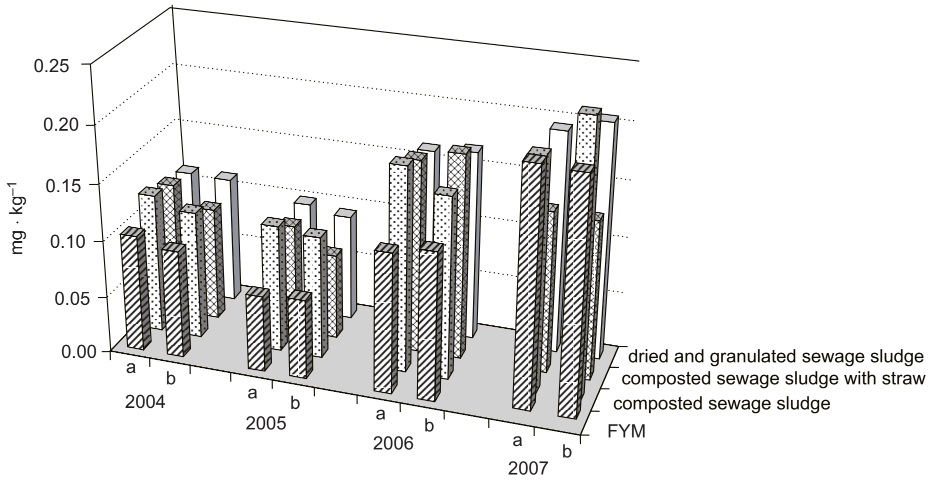

Fig. 2. Content of Cd in soil after harvest; explanations as under Table 1

After four years, the amount of soluble lead in soil sampled from the objects fertilized with dried and granulated sludge was significantly lower (on average 9.96 mg · kg^{-1}) compared with the other objects. In contrast, the introduction of FYM or composted sludge, which contained less Pb, resulted in the fertilized soil containing, on average, from 10.13 to 10.72 mg Pb · kg^{-1}. Krzywy et al [11], who analysed chemical composition of sewage sludge and sludge composts, found out that an addition of straw to such fertilizers depressed the content of heavy metals, therefore such composts could be used in farming.

Among the biowaste fertilizers tested in presented experiment, the highest cadmium content was found in sewage sludge and sludge composts, which significantly affected the content of this heavy metal in soils amended with these organic fertilizers (Table 2). After four years of the trials, the highest level of cadmium was determined in the objects fertilized with composted and dried sewage sludge (on average, 0.15 and 0.16 mg · kg^{-1}, respectively). In 2007, a significant increase in the Cd soil concentration was observed: 75 % more cadmium compared with 2004 and over two-fold more than in 2005, which can suggest that the mobile form of this element had been activated.

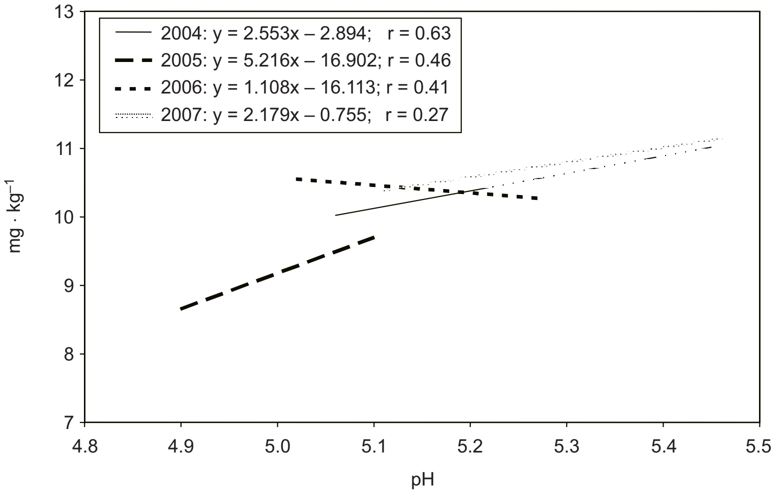

Fig. 3. Dependence between soil reaction and content of Pb

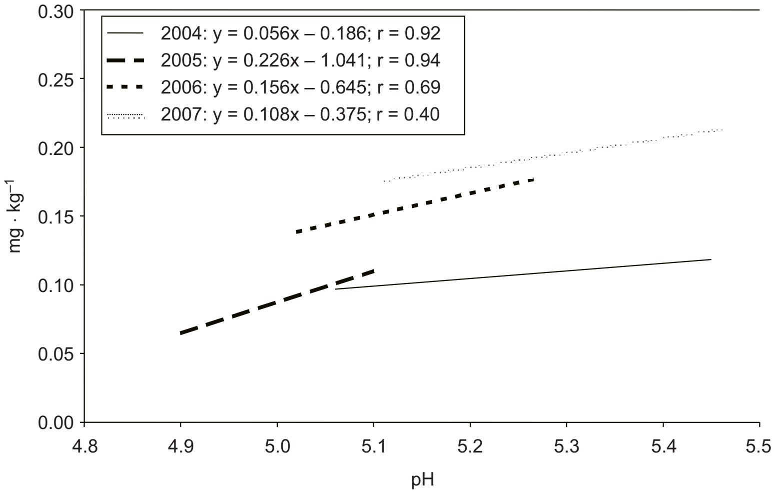

Fig. 4. Dependence between soil reaction and content of Cd

Weber et al [9] also claim that the content of heavy metals in soil depends on the type of compost introduced and type of soil. Pinamonti et al [10] conducted a six-year study on the effect of composts on soil and plant characteristics, in which they proved that although the examined trace elements had not produced any toxic effect on the growth and development of plants, the amounts of zinc, copper, nickel, lead, cadmium and chromium in the test soils had risen.

The analysis of correlation and regression of our results has demonstrated that the content of lead in soil was less depended ($r = 027–0.63$) on the soil reaction than that of cadmium ($r = 0.40–0.94$) (Fig. 3 and 4). However, Piotrowska and Terelak [11] concluded that correlation coefficients for cadmium and soil reaction were low and did not indicate any significant relationship.

Conclusions

1. Soil fertilization with sewage sludge or composts introduced in a dose of 10 Mg d.m. $\cdot$ ha^{-1} raises the soil pH only in the year when these fertilizers are applied. It seems more advantageous to use biowaste fertilizers twice during a crop rotation system 5 Mg d.m. $\cdot$ ha^{-1}, each.
2. The content of available lead in soil is modified to a greater extent by the type of biowaste fertilizers than the application method, whereas the content of cadmium in soil is additionally affected by a dose of sewage sludge or sludge composts.
3. Using municipal biowaste for soil fertilization increases the soil content of mobile forms of lead and cadmium but does not result in the amounts of these trace elements exceeding the geochemical background.

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ZAWARTOŚĆ ROZPUSZCZALNYCH FORM OŁOWIU I KADMU W GLEBIE NAWOŻONEJ KOMPOSTAMI Z OSADÓW ŚCIEKOWYCH

[1] Katedra Chemii Rolnej i Ochrony Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie
[2] Katedra Gleboznawstwa i Ochrony Gleb
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: W latach 2004–2007 w Zakładzie Produkcyjno-Doświadczalnym Bałcyny koło Ostródy na glebie płowej typowej wytworzonej z gliny lekkiej zwałowej, o dużej zawartości przyswajalnego P, średniej K i małej Mg, przeprowadzono doświadczenie w 4-polowym płodozmianie (ziemniak, jęczmień jary, rzepak ozimy, pszenica ozima). Doświadczenie założone metodą losowanych bloków obejmowało 8 obiektów (2 serie po 4 obiekty): 1. obornik, 2. komunalny osad ściekowy kompostowany ze słomą (z Iławy), 3. osad ściekowy suszony i granulowany (z Iławy), 4. osad ściekowy kompostowany (z Ostródy). W I serii komposty i obornik zastosowano jednorazowo (2004 r.) w dawce 10 Mg s.m. $\cdot$ ha^{-1}, a w pozostałych latach tylko nawożenie mineralne. W 2 serii nawozy te stosowano ilości 5 Mg s.m. $\cdot$ ha^{-1} pod ziemniak i 5 Mg s.m. $\cdot$ ha^{-1} pod rzepak ozimy). Na obiektach z nawozami organicznymi i obornikiem, w zależności od zawartości w nich N-ogółem, azot został zbilansowany w 2004 r. do 150 kg $\cdot$ ha^{-1}, a w 2005 r. do 120 kg $\cdot$ ha^{-1}. Pod jęczmień jary i pszenicę ozimą stosowano tylko nawożenie mineralne. Przez cztery lata badań stwierdzono niewielki wzrost zawartość Pb i Cd w glebie użyźnianej kompostami z osadów ściekowych w porównaniu z glebą nawożoną obornikiem. Analiza gleb po zbiorze roślin wykazała, że zawartość tych metali w glebie nie przekracza wartości określanych jako zawartość naturalna. Dla Pb wartości te wahały się średnio od 8,9 do 11,2 mg $\cdot$ kg^{-1}, a dla Cd od 0,10 do 0,22 mg $\cdot$ kg^{-1}.

Słowa kluczowe: osady ściekowe, gleba, ołów, kadm

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Wojciech DĄBROWSKI[1]

CONTENTS OF ALKALINE CATIONS IN SLUDGE FROM DAIRY WASTEWATER TREATMENT PLANT

ZAWARTOŚĆ KATIONÓW ZASADOWYCH W OSADACH Z OCZYSZCZALNI ŚCIEKÓW MLECZARSKICH

Abstract: The dairy processing plants, that in majority use individual wastewater treatment plants and sewage sludge processing systems, dominate in Podlasie province. Those works have an enormous influence on aqueous and soil environments. In total, nine individual dairy wastewater treatment plants operate in the province, and they process from 600 to 5500 m^3 of sewage daily, while amount of excessive sludge generated during the treatment process is 90 to 2200 Mg of dry matter, annually. The sludge recycling into the environment in a form of fertilizers is possible due to low levels of heavy metals in relation to requirements set by a decree on municipal sewage sludge. Contents of nutrients such as Ca, Mg, K, and Na (alkaline cations) are one of the most important factors that make possible to apply sewage sludge generated during dairy wastewater treatment; however, the legal acts require only calcium and magnesium determination. The paper presents results of these elements determinations in two dairy wastewater treatment plants in Podlasie province. Both plants apply different ways for sludge aerobic stabilization. That study is a part of the research project "Evaluation of constructed wetlands usefulness to purify reject water from sludge aerobic processing in dairy wastewater treatment plants".

Keywords: sewage sludge, alkaline cations, sludge recycling

Sewage sludge and reject water are by-product from every wastewater treatment plants that applies sludge activated system. The recycling of sewage sludge generated in dairy wastewater treatment plants is determined by principal physicochemical as well as sanitary parameters; appropriate procedures determining its agricultural application have to be met. According to legal definitions, sludge is a waste. Besides concentrations of selected heavy metals, legal acts predicted the necessity of determining nitrogen, phosphorus, calcium, and magnesium in sewage sludge [1]. The sludge composition depends on many factors, including the most important: sewage type and their processing way. Sludge produced in agricultural and foodstuff wastewater treatment plants are more useful for fertilizing.

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[1] Department of Technology in Engineering and Environmental Protection, Białystok University of Technology, ul. Wiejska 45a, 15–351 Białystok, Poland, phone 85 746 9644, email: dabrow@pb.bialystok.pl

The dairy processing plants, that in majority use individual sewage treatment and sewage sludge processing systems, dominate in Podlasie province. Those works have an enormous influence on aqueous and soil environments. In total, nine individual dairy wastewater treatment plants operate in Podlasie province, and they process from 600 to 5500 m^3 of sewage daily, while amount of excessive sludge generated during the treatment process is 90 to 2200 Mg of dry matter annually. All analyzed individual dairy plants stabilize sludge in aerobic-simultaneous way or in separate chambers [2]. Development of factories makes the increase of sewage loads, which results in the amount of generated sludge. There is a necessity for their safe final utilization. Sludge produced in agricultural and foodstuff wastewater treatment plants is more useful for fertilizing; that from municipal plants often does not meet the sanitary criterion and may contain significant amounts of heavy metals [3].

The study was aimed at evaluating the usefulness of sludge from dairy wastewater treatment plant for soil fertilizing in respect of alkaline cations – potassium, magnesium, sodium, and calcium content.

Material and methods

Study was carried out in two dairy wastewater treatment plants in Podlasie province. Sewage sludge is aerobically stabilized in both objects: that in Wysokie Mazowieckie applies separated stabilization, the other in Bielsk Podlaski stabilizes sludge simultaneously with purification process. Wysokie Mazowieckie is one of the largest and the most advanced dairy treatment plant in Poland. Grit chamber and step-wise bars work in mechanical part, while system for intensive biogenic compounds removal by means of biological and chemical methods is introduced in biological part. Sludge is mechanically concentrated, aerobically stabilized in separated chambers at 30–36 ^{o}C, and then dehydrated in a press. Reject water generated during the aerobic stabilization is directed to the well and are returned to the purification cycle behind the grit chamber.

Wastewater treatment plant in Bielsk Podlaski was built in the mid of 70's. The purification process is based on the circulation ditches working exclusively in aerobic system (PROMLECZ system) and vertical sedimentation tanks. The purification line is completed by the chamber for preliminary aeration and installation for phosphorus precipitation. Chamber for sludge regeneration and gravitational thickener works in sedimentation section. By 2005, sludge was dehydrated on sludge drying beds, while at present after thickening, they are directed for agricultural use.

Figures 1 and 2 present schemes of both wastewater treatment plants, where studies were performed.

Sludge samples have been collected since January till December 2007. In total, 12 determination series (including K, Na, Ca, Mg and organic substances) were made. At the same time, heavy metals were determined in samples (results are not presented in this study). Similar analyses were also conducted in raw wastewater and reject water from sludge treatment. Studies were completed with evaluation of organic matter determination in the sludge to find out their stabilization level, which is important parameter determining the possibilities and directions of its final utilization.

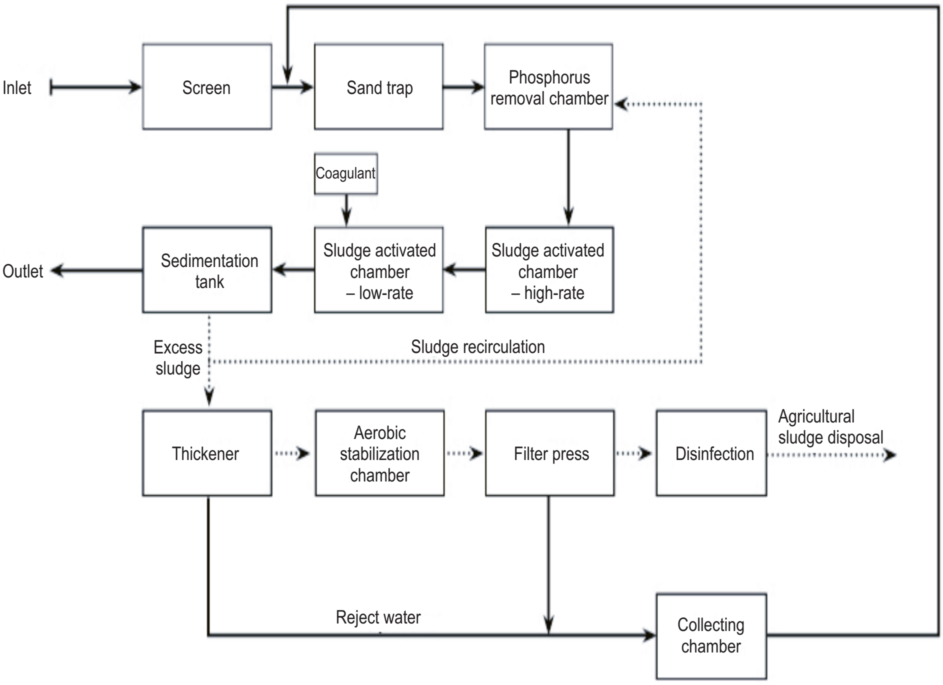

Fig. 1. Wysokie Mazowieckie WWTP – schematic flow

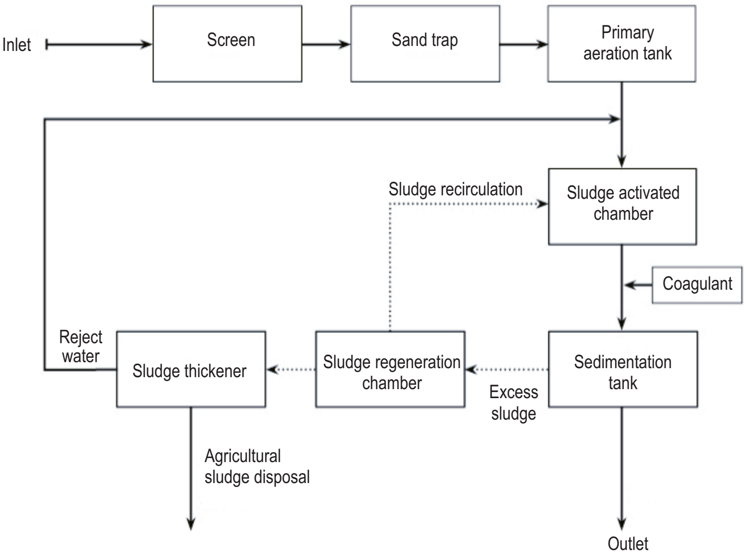

Fig. 2. Bielsk Podlaski WWTP – schematic flow

Microelement contents were determined by certified laboratory in accordance to norm PN-EN ISO 11885 using optical emission spectrometer with inductively-coupled plasma (Varian Vista MPX). Achieved results were compared with those from 1998–2000 within the program "Sewage and sludge balance in wastewater treatment plants of Podlasie province in 1998–2000". Those study included 98 wastewater treatment plants localized in Podlasie province and referred both to municipal and industrial wastewater treatment plants [4].

Results and discussion

Result from sewage sludge determination is presented in Table 1. The table also includes results related to sludge from municipal wastewater treatment plants in Podlasie province, liquid and organic manure [5]. Such result presentation is aimed at indicating that sewage sludge can be potential substitute of natural organic fertilizers.

Table 1

Contents of K, Na, Ca and Mg [g · kg^{-1} d.m.] and organic substances [g · kg^{-1} d.m.] in stabilized sludge and liquid and organic manure

Parameter	K	Na	Ca	Mg	Organic substances
Sensitivity limit	0.1	0.2	0.8	0.1	
Wysokie Mazowieckie					
Minimum	5.30	2.12	16.23	3.22	72.1
Maximum	14.80	7.68	26.89	5.67	861.8
Arithmetic mean	9.10	3.61	21.44	4.39	804.2
Median	9.08	3.16	20.79	4.60	802.3
Standard deviation	2.61	1.61	3.52	0.61	48.0
Bielsk Podlaski					
Minimum	8.75	15.31	21.30	2.56	413.2
Maximum	12.54	21.24	41.23	5.87	722.0
Arithmetic mean	9.70	18.45	31.07	4.21	571.2
Median	9.21	19.30	30.92	4.12	582.5
Standard deviation	1.28	1.86	4.11	0.84	81.2
Municipal sludge-mean [4]	9.54	2.55	69.42	19.90	605.4
Liquid maure	14.64	3.91	28.82	13.17	800.0
Organic manure [5]	35.60	5.4	17.80	14.60	500.0

Analysis of achieved results revealed that potassium, calcium, and magnesium contents in sediments were similar in both purification plants that used different ways for aerobic sludge stabilization. The same referred to raw sewage flowing into both dairy wastewater treatment plants. The only differences were recorded in the case of sodium. When comparing results for dairy sludge with those for municipal wastewater treatment plants, much more calcium was found in the latter. It was due to the fact that many wastewater treatment plants are forced to apply sludge hygienization using lime.

It is necessary in the case of plants, to which sewage are supplied by meat processing works, hospitals, etc. In such cases, methods of thermal sludge processing should be used; their possibilities and ranges are in practice well recognized and applied in real scale [6]. However, studies upon the sanitary status of sewage sludge from dairy sewage treatment plants made at the beginning of 90's did not indicate the necessity for their hygienization. It results from the character of sewage produced by dairy works, where very strict quality norms for production process, raw materials used, and final products must be met. In consequence, the sewage sludge meets sanitary criteria for its agricultural utilization [7].

Filipek and Fidecki [8] also achieved similar results when studying sewage sludge from dairy wastewater treatment plants: potassium (4.6–18.5 g · kg^{-1} d.m.), calcium (3.0–46.9 g · kg^{-1} d.m.), sodium (3.2–4.6 g · kg^{-1} d.m.), magnesium (4.5–6.2 g · kg^{-1} d.m.). Here recorded results upon the sewage sludges do not differ from those presented by other authors [6, 8, 9]. According to research performed at University of Agriculture in Krakow, sewage sludge from municipal wastewater treatment plant was characterized by following contents of macronutrients: potassium (3–3.9 g · kg^{-1} d.m.), calcium (44.9–89.3 g · kg^{-1} d.m.), sodium (3.0–16.0 g · kg^{-1} d.m.), magnesium (4.2–6.2 g · kg^{-1} d.m.) [5].

Table 2

Contents of K, Na, Ca and Mg [g · kg^{-1}] in raw wastewater – Wysokie Mazowieckie and Bielsk Podlaski wastewater treatment plant

Parameter	K	Na	Ca	Mg
Sensitivity limit	0.4	0.1	0.8	0.1
Wysokie Mazowieckie				
Minimum	46.60	266.54	133.79	23.42
Maximum	49.34	278.57	176.56	29.64
Arithmetic mean	48.29	274.48	167.93	27.72
Median	48.66	276.34	174.36	28.63
Standard deviation	0.94	4.46	14.34	2.07
Bielsk Podlaski				
Minimum	49.97	20.85	94.37	20.85
Maximum	58.97	31.23	112.34	31.23
Arithmetic mean	56.54	339.60	106.39	27.97
Median	57.60	328.47	111.05	29.92
Standard deviation	3.15	26.09	7.29	3.76

Comparison of results for sewage sludge with liquid and organic manure confirms the advisability of utilizing stabilized sludge from dairy wastewater treatment plants as a fertilizer. Analyzed sewage sludge contained much less potassium and magnesium than manure, similar amounts of calcium, and slightly less sodium. Presented results for sewage (Table 2) were aimed at indicating the dependencies between these elements contents in sewage and sludge regardless the way of sewage treatment and sludge processing. The composition of sewage was very similar in both cases, as well as for reject water from sludge treatment. Macronutrients contained in the sludge may – in the case of plants – improve their water balance, accelerate photosynthesis processes, enhance the productivity of soil fertilized with the sludge. In the case of wastewater treatment plant in Wysokie Mazowieckie, it was found that processed sludge contained large amounts of organic matter (804.2 $g \cdot kg^{-1}$, on average) in relation to 571.2 $g \cdot kg^{-1}$ in Bielsk Podlaski. It may prove that stabilization process requires interference (intensification) to decrease the organic matter content in final product. It is when sludge processing technology is analyzed separately from its final application. On the other hand, when taking into account the agricultural utilization of sludge from dairy wastewater treatment plants, it is not necessary to decrease organic matter level below 50 %, which is accepted in literature for stabilized sludge.

Conclusions

1. Macronutrients contents in stabilized sludge from dairy wastewater treatment plant predispose it for agricultural application.
2. Calcium and sodium contents in sludge were similar to those in liquid and organic manure, while those of potassium and magnesium were much lower.
3. The way of aerobic stabilization did not significantly affect the macronutrients contents in stabilized sludge, and their amounts resulted from the sewage type.
4. Increasing the sludge stabilization level can be achieved by changing the process parameters such as load, temperature and retaining time.
5. There is no need to apply advanced and expensive method for processing the sewage sludge from dairy wastewater treatment plants, and those methods should be applied in the case of sludge from municipal wastewater treatment plants.

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ZAWARTOŚĆ KATIONÓW ZASADOWYCH W OSADACH Z OCZYSZCZALNI ŚCIEKÓW MLECZARSKICH

Katedra Technologii w Inżynierii i Ochronie Środowiska
Politechnika Białostocka

Abstrakt: Na terenie województwa podlaskiego dominują zakłady przetwórstwa mleczarskiego, które w większości korzystają z indywidualnych systemów oczyszczania ścieków i przeróbki osadów ściekowych. Zakłady te mają duży wpływ na stan środowiska wodnego i glebowego regionu. Na terenie województwa podlaskiego działa dziewięć indywidualnych oczyszczalni ścieków mleczarskich oczyszczających od 600 do 5500 m^3 ścieków na dobę, ilość osadów nadmiernych generowanych w trakcie procesu oczyszczania ścieków wynosi od 90 do 2200 Mg suchej masy w ciągu roku. Recykling osadów do środowiska w postaci nawozu jest możliwy dzięki małej zawartości metali ciężkich w stosunku do wymagań stawianych przez Rozporządzenie Ministra Środowiska w sprawie komunalnych osadów ściekowych. Jednym z ważnych czynników umożliwiających stosowanie osadu ściekowego generowanego w czasie oczyszczania ścieków mleczarskich jest zawartość pierwiastków nawozowych: Ca, Mg, K i Na, z których ustawodawca wymaga jedynie określenia zawartości wapnia i magnezu. W pracy przedstawiono wyniki badań tych pierwiastków przeprowadzonych w dwóch oczyszczalniach ścieków mleczarskich zlokalizowanych na terenie województwa podlaskiego. Stosują one odmienny sposób stabilizacji tlenowej osadów. Wykonane badania są częścią projektu badawczego „Określenie przydatności złóż hydrofitowych do oczyszczania odcieków z tlenowej przeróbki osadów w oczyszczalniach ścieków mleczarskich”.

Słowa kluczowe: osady ściekowe, kationy zasadowe, recykling osadów

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Magdalena DZIĘGIELEWSKA[1], Grażyna KAUP[2]
and Anna KIEPAS-KOKOT[3]

INFLUENCE OF DIVERSE TEMPERATURE AND MOISTURE ON THE PUPAE OF *Cameraria ohridella*

WPŁYW ZRÓŻNICOWANEJ TEMPERATURY I WILGOTNOŚCI NA POCZWARKI SZROTÓWKA KASZTANOWCOWIACZKA *Cameraria ohridella*

Abstract: On the basis of research carried out during the composting of horse-chestnut leaves diseased by *Cameraria ohridella* it was found that the temperature and moisture of the ground may considerably influence viability of pupae of this pest. The survivability of *Cameraria ohridella* pupae kept in ripe leaf compost of different levels of moisture and in diverse thermal conditions was tested in laboratory conditions. The following variants of ground-moisture were adopted: 25 % – dry state, 35–40 % – fresh state, 50 % – wet state. The temperature at which the tests were performed was as follows: 10 °C, 20 °C and 40 °C. At the temperature of 10 °C the survivability of pupae was strongly correlated with the moisture of the ground and dropped with the decrease of moisture. It was found that there occurred nearly 100 % pupae mortality in a variant with dry ground after one month's exposition in dry leaves. In variants with increased moisture the majority of pupae (70–80 %) preserved the ability to further development. At the temperature of 20 °C distinct limiting of *Cameraria ohridella* viability was observed in extreme variants of the experiment (dry and wet states); and, what is important, wet environment affected the increase of mortality of pupae more effectively. At the temperature of 40 °C, in all variants, with diversified moisture, 100 % pupae mortality of the harmful butterfly was observed.

Keywords: horse chestnut leafminer *Cameraria ohridella*, temperature, moisture, pupae morality

The control of *Cameraria ohridella* is of a very complex nature [1–3]. It ranges from chemical methods based on direct spraying of trunks and crowns of trees and on microinjection to mechanical control by means of bands and raking and composting leaves with hibernating pupae.

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[1] Department of Plant Protection, West Pomeranian University of Technology in Szczecin, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, phone 91 449 63 74, fax 91 /442 56 90, email: entomology@agro.ar.szczecin.pl

[2] Department of Agronomy, West Pomeranian University of Technology in Szczecin, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, phone 91 449 63 05, email: Grazyna.Kaup@zut.edu.pl

[3] Department of Protection and Management of Environment, West Pomeranian University of Technology in Szczecin, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, phone 91 449 63 53, email: Anna.Kiepas-Kokot@zut.edu.pl

Research results of the mortality of the pupae of *Cameraria ohridella* during composting in piles with diseased leaves of chestnut [4] show that the factor that determines the sanitation degree of leaves is their low moisture, which is helped by high temperature. In the majority of research works from this field only the influence of temperature, of which increase to 40 °C results in death of all pupae, is highlighted [5, 6]. During the composting of leaves, however, it is important to keep high moisture (60–70 %), which ensures the proper course of the process. Such action has a protective character for *Cameraria ohridella* pupae and enables them to survive the hot stage of composting. What is more, autumn composting of leaves in compost piles, because of the impact of low air temperature, does not occur with considerable temperature increase characteristic for easily decomposing organic mass, with the maximum temperature at the level of 60 °C. In such a situation there remains to seek such solutions which will make possible the right course of the composting process and full sanitation. Arnold and Sengonca [7] report that mechanical breaking up of leaves during the composting of diseased leaves of chestnut works as an auxiliary action in the control of the pupae of *Cameraria ohridella.* Taking all above-mentioned factors into account one should work out combinations that would make possible reaching satisfactory level of the number of living pupae, and even their full elimination.

The aim of the research was to determine optimal moisture and thermal conditions of leaf compost piles in order to effectively control the hibernating pupae of *C. ohridella.*

Materials and method

To verify the suggested thesis, that increased moisture of the environment of the pupae hibernation works as a protection from destructive action of increased temperature, an experiment was set. The experiment investigated the viability of *Cameraria ohridella* pupae kept in ripe leaf compost of different moisture levels and in different thermal conditions.

The moisture of the ground: 25 % (dry state), 35–40 % (fresh state), 50 % (wet state). The temperature of storing samples: 10 °C, 20 °C, 40 °C.

Three variants of the experiment were employed:

1. In the stable temperature of 10 °C, samples of compost of diverse moisture (dry, fresh and wet) were stored with the pupae of *C. ohridella* in the number of 60, in each variant (with the division into 3 repetitions).
2. In the stable temperature of 20 °C, samples of compost of diverse moisture (dry, fresh and wet) were stored with the pupae of *C. ohridella* in the number of 60, in each variant (with the division into 3 repetitions).
3. In the stable temperature of 40 °C, samples of compost of diverse moisture (dry, fresh and wet) were stored with the pupae of C. *ohridella* in the number of 60, in each variant (with the division into 3 repetitions).

In the compost the pupae of *Cameraria ohridella* of a hibernating generation selected from leaves left after preying of the pest in one of green areas in Szczecin were exposed. After one-month exposition in determined moisture and thermal conditions, among 20 pupae used in each repetition, the number of living and dead pupae, including those infected with mould, was found. The experiments were carried out in 3 repetitions (A, B, C) and the obtained results, due to the high individual variation of reaction were presented for all performed repetitions without averaging the obtained results.

Results

At the temperature of 10 ^{o}C (average for a winter period) the condition of pupae in compost was highly correlated with the moisture of the ground (Table 1). The survivability of the pupae decreased together with the drop of moisture. In the variant of dry ground after one-month exposition, out of 60 pupae only one survived. A considerable part of the pupae decomposed, which made impossible their finding. A big part of the pupae moulded, which soon resulted in their disappearance. In moist variants a bigger part of the pupae kept the ability to develop and its change depended on the length of temperature operation.

Table 1

The viability of the pupae of *Cameraria ohridella* (out of 20 individuals used in a repetition) at the temperature of 10 ^{o}C, with diverse compost moisture

Dry compost variant			
Repetition	A	B	C
Number of individuals	7	12	8
Number of living individuals	0	1	0
Number of dead individuals	7	11	8
Moulded individuals (among the above-mentioned)	6	11	8
Fresh compost variant			
Repetition	A	B	C
Number of individuals	8	10	8
Number of living individuals	4	5	6
Number of dead individuals	4	5	2
Moulded individuals (among the above-mentioned)	3	2	0
Wet compost variant			
Repetition	A	B	C
Number of individuals	20	20	20
Number of living individuals	10	15	16
Number of dead individuals	10	5	4
Moulded individuals (among the above-mentioned)	7	0	0

In the temperature of 20 ^{o}C effective control of *C. ohridella* was observed in marginal variants of the experiment (dry and wet ones); wet environment in this temperature was more effective in reducing the pupae of *C. ohridella* (Table 2).

Table 2

The viability of the pupae of *Cameraria ohridella* (out of 20 individuals used in a repetition) at the temperature of 20 °C, with diverse compost moisture

Dry compost variant			
Repetition	A	B	C
Number of individuals	10	4	12
Number of living individuals	0	0	0
Number of dead individuals	10	4	12
Moulded individuals (among the above-mentioned)	6	0	4
Fresh compost variant			
Repetition	A	B	C
Number of individuals	5	7	6
Number of living individuals	5	0	2
Number of dead individuals	0	7	4
Moulded individuals (among the above-mentioned)	0	0	0
Wet compost variant			
Repetition	A	B	C
Number of individuals	0	0	0
Number of living individuals	0	0	0
Number of dead individuals	0	0	0
Moulded individuals (among the above-mentioned)	0	0	0

At the temperature of 40 °C, 100 % mortality and decomposition of horse chestnut leafminer after the exposition of one month was stated (Table 3).

Table 3

The viability of the pupae of horse chestnut leafminer (out of 20 individuals used in a repetition) at the temperature of 40 °C, with diverse compost moisture

Dry compost variant			
Repetition	A	B	C
Number of individuals	0	0	0
Fresh compost variant			
Repetition	A	B	C
Number of individuals	0	0	0
Wet compost variant			
Repetition	A	B	C
Number of individuals	0	0	0

The variant of the experiment with the ambient temperature of 10 °C ought to be considered the closest to the temperature of autumn and winter storing of leaves. Thus, it is necessary to rake fallen chestnut leaves in a dry state (not exceeding the moisture of 25 %). The storage of raked leaves have to make impossible the contact with rainwater eg with use of plastic bags or covering with plastic film. Such wintering of leaves guarantees high mortality of pupae of the pest. Next year in spring one should start composting, transforming leaves into the form of leaf compost, for the use in green area maintenance. Basing on the experience of German scientists, one can increase the chance of full destruction of the pupae occurring in leaves through mechanical breaking up of leaves. It causes death of 20 % of pupae occurring in leaves and at the same time it destroys their shields, exposing the pupae to direct contact with the environment.

Conclusions

1. The research results point to the occurrence of the relation between moisture and temperature of the ground causing the dying of *Cameraria ohridella* pupae.
2. The relation between these factors revealed itself most strongly in the lowest of the tested temperatures (10 °C). The survivability of the pupae decreased with the drop of moisture.
3. Composting leaves in a compost pile in the autumn-winter season, with low ambient temperatures should be preceded with the storing of leaves for one month in limited moisture (25 %).

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WPŁYW ZRÓŻNICOWANEJ TEMPERATURY I WILGOTNOŚCI NA POCZWARKI SZROTÓWKA KASZTANOWCOWIACZKA *Cameraria ohridella*

[1] Zakład Ochrony Roślin
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie
[2] Katedra Agronomii
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie
[3] Katedra Ochrony i Kształtowania Środowiska
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

Abstrakt: Na podstawie badań przeprowadzonych podczas kompostowania liści kasztanowca, porażonych przez szrotówka kasztanowcowiaczka, wykazano że temperatura i wilgotność podłoża mogą znacznie wpływać na żywotności poczwarek tego szkodnika. W warunkach laboratoryjnych badano przeżywalność poczwarek szrotówka przetrzymywanych w dojrzałym kompoście liściowym, o różnym poziomie uwilgotnienia i w zróżnicowanych warunkach termicznych. Przyjęto następujące warianty uwilgotnienia podłoża: 25 % (stan suchy), 35–40 % (stan świeży), 50 % (stan mokry). Temperatura, w której wykonywano testy, wynosiła odpowiednio: 10 °C, 20 °C i 40 °C. W temperaturze 10 °C przeżywalność poczwarek była silnie skorelowana z wilgotnością podłoża i malała wraz ze spadkiem wilgotności. W wariancie z podłożem suchym zanotowano prawie 100 % śmiertelność poczwarek, po miesięcznej ekspozycji w suchych liściach. W wariantach ze zwiększoną wilgotnością większość poczwarek (70–80 %) zachowała zdolność do dalszego rozwoju. W temperaturze 20 °C wyraźne ograniczenie żywotności szrotówka zaobserwowano w skrajnych wariantach doświadczenia (stan suchy i mokry), przy czym mokre środowisko skuteczniej wpływało na wzrost śmiertelności poczwarek. W temperaturze 40 °C, we wszystkich wariantach, przy zróżnicowanej wilgotności, zanotowano 100 % śmiertelność poczwarek szkodliwego motyla.

Słowa kluczowe: szrotówek kasztanowcowiaczek, temperatura, wilgotność, śmiertelność poczwarek

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Magdalena FRĄC[1] and Stefania JEZIERSKA-TYS[2]

CHANGES IN MICROBIOLOGICAL ACTIVITY OF SOILS FERTILISED WITH VARIED DOSES OF SLUDGE FROM A DAIRY SEWAGE TREATMENT PLANT

ZMIANY AKTYWNOŚCI MIKROBIOLOGICZNEJ GLEB NAWOŻONYCH ZRÓŻNICOWANYMI DAWKAMI OSADU Z OCZYSZCZALNI ŚCIEKÓW MLECZARSKICH

Abstract: The influence of dairy sewage sludge on some microbiological characteristics was studied. The experiment was carried out in laboratory conditions. Microbiological analyses were following: respiration activity and numbers of some groups of microorganisms. Different doses of dairy sewage sludge were applied into brown and grey-brown podzolic soils. The effect of the sludge on the microbial groups under study depended on the dose of the sludge, on the type of soil, and on the kind of microbiological parameter.

Keywords: dairy sewage sludge, microorganisms, respiration activity, soil

Soil is a medium in which numerous and diverse biological, chemical and physical processes take place, the run of which is affected by anthropogenic factors [1]. Microorganisms inhabiting the soil environment play a crucial role in the decomposition of soil organic matter (SOM) and in the circulation of elements, therefore the microbiological activity is used for the estimation of the ecological condition of soils [2, 3]. Microorganisms are involved in the main processes taking place in soil, ie humification, recycling or mineralisation of organic wastes, making the biogens contained in them available to plants [4–7]. The presence of certain microbial groups with known ecological requirements, eg nitrifying or cellulolytic bacteria, is considered to constitute microbiological indicators [8, 9]. Biodiversity of microorganisms in soil is important for maintaining health of the environment and for improvement of yields of crop plants [10, 11].

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[1] Department of Study the Soil-Plant System, Institute of Agrophysics of Polish Academy of Sciences in Lublin, ul. Doświadczalna 4, 20–290 Lublin 27, phone 81 744 5061, ext. 156, email: m.frac@poczta. fm

[2] Department of Agricultural Microbiology, University of Life Sciences in Lublin, ul. Leszczyńskiego 7, 20–069 Lublin, phone 81 532 3047, ext. 161, email: stefania_tys@op.pl

In recent years a notable increase has been observed in the agricultural utilisation of sewage sludge, including sludge originating from the agricultural-food industry. Therefore, monitoring of changes in the microbiological activity of soils fertilised with such wastes appears to be important, considering the quality and health status of soils as well as the economic aspects.

Material and methods

The pot experiment was set up on two different types of soil (brown and grey-brown podzolic). The brown soil, developed from a silty clay formation, was characterised by the following grain size composition: 8 % of sand fraction (1.0–0.1 mm), 47 % of silt fraction (0.1–0.02 mm) and 45 % of fine particles (< 0.02 mm). The grey-brown podzolic soil, developed from strongly loamy sand, had the following grain size composition: 65 % of sand fraction (1–0.1 mm), 19 % of silt fraction (0.1–0.02 mm) and 16 % of fine particles (< 0.02 mm). The basic characteristics of the soils and dairy sewage sludge used in the experiments are given in Table 1. Each pot contained 4 kg of brown or grey-brown podzolic soil mixed with appropriate dose of dairy sewage sludge. The experiment comprised the following treatments 1 kg of soil: 1 – control soil, without fertilisation; 2 – 10 g of dairy sewage sludge; 3 – 20 g of dairy sewage sludge; 4 – 26.7 g of dairy sewage sludge; 5 – 40 g of dairy sewage sludge; 6 – 66.7 g of dairy sewage sludge; 7 – 100 g $\cdot$ kg^{-1} of dairy sewage sludge and 8 – 200 g of dairy sewage sludge.

Table 1

Characteristics of soils and dairy sewage sludge

Measurements	Unit	Brown soil	Grey-brown podzolic soil	Dairy sewage sludge
pH	[-]	6.4	4.8	8.5
C	[g $\cdot$ kg^{-1} d.m.]	13.5	4.5	400
N		1.6	0.4	33.2
C/N	[-]	8.3	12.5	12.0
P	[g $\cdot$ kg^{-1} d.m.]	18.3	5.3	11.5
K		26.8	8.7	2.5

The soil was watered to 60 % of the maximum water capacity. Incubation was conducted at room temperature, for 8 months, under conditions of controlled moisture. Microbiological and biochemical analyses were made after 14, 30, 60, 90, 120 and 240 days of the experiment. Microbiological analyses of the soil material included the following determinations: respiration activity, with the method of Rühling and Tyler [12], so-called total number of bacteria with low nutritional requirements (oligotrophic bacteria), on substrate with soil extract and K_2HPO_4 [13], so-called total number of filamenous fungi, on Martin substrate [14], number of cellulolytic bacteria, on liquid substrate [13], number of "proteolytic" bacteria and fungi, on Frazier substrate with gelatine [13], number of ammonising bacteria, on liquid substrate with peptone [13], number of nitrifying bacteria, on liquid mineral substrate [13].

To determine the effect of the experimental treatments, duration of the experiment, and types of soils used in the pot experiment on the values of the microbiological features under study, three-factor analyses of variance were performed. Mean values of the studied features for the treatments, times of incubation and soil types were compared using Tukey 95 % intervals of confidence at the level of significance $\alpha = 0.05$. Statistical processing of the results was performed by means of the Statistica 7.1 software. No analysis of variance was performed for the umbers of cellulolytic, ammonising and nitrifying bacteria, as calculation of the numbers of those microbial groups was made with the use of McCrady's Tables based on the principles of mathematical statistics.

Results

The total periodic respiratory activity in the studied soils, measured by the amount of emitted carbon dioxide, is illustrated in Fig. 1. The performed analysis of variance showed that the application of varied doses of dairy sewage sludge in the experiment had a significant effect on the average level of carbon dioxide emission from both soils; an increase in CO_2 emission was noted with increasing doses of sludge introduced in the soil. A significant decrease was observed in carbon dioxide emission from both soils with the duration of the experiment. Statistical analysis did not reveal any significant differences in carbon dioxide emission between the two soils under study.

The study showed notable periodic variation in the number of oligotrophic bacteria (Fig. 1). Analysis of variance revealed growth of the studied microorganisms that intensified with increase in the doses of sludge introduced in the soil. The number of bacteria decreased significantly with the time of the experiment. Greater numbers of the studied microbial groups were characteristic of the brown soil.

The periodic numbers of fungi in the brown and grey-brown podzolic soils with different doses of dairy sewage sludge are presented in Fig. 2. Analysis of variance showed that the highest numbers of the studied fungi were characteristic of treatments 3, 4 and 5, ie those with sludge doses of 20, 26.7 and 40 $g \cdot kg^{-1}$ of soil, respectively. As in the case of bacteria, a significant decrease in the numbers of fungi was observed with the duration of the experiment. A higher number of fungi was found in the grey-brown podzolic soil compared with the brown soil.

As a result of the performed analyses it was found that the applied doses of dairy sewage sludge had differing effect on the numbers of cellulolytic bacteria, depending on the type of soil and on the period of the experiment (Fig. 2). All the doses of the sludge, with the exception of the highest (100 and 200 $g \cdot kg^{-1}$), caused stimulation of the growth of the microbial group under study.

The number of bacteria mineralising cellulose under aerobic conditions decreased during the period of the experiment. In the grey-brown podzolic soil a greater number of those bacteria was observed than in the brown soil.

The results presented in Fig. 3 indicate that the applied doses of the sludge had a significant effect on the numbers of proteolytic bacteria in both studied soils. As in the case of the total number of bacteria, the number of proteolytic bacteria increased

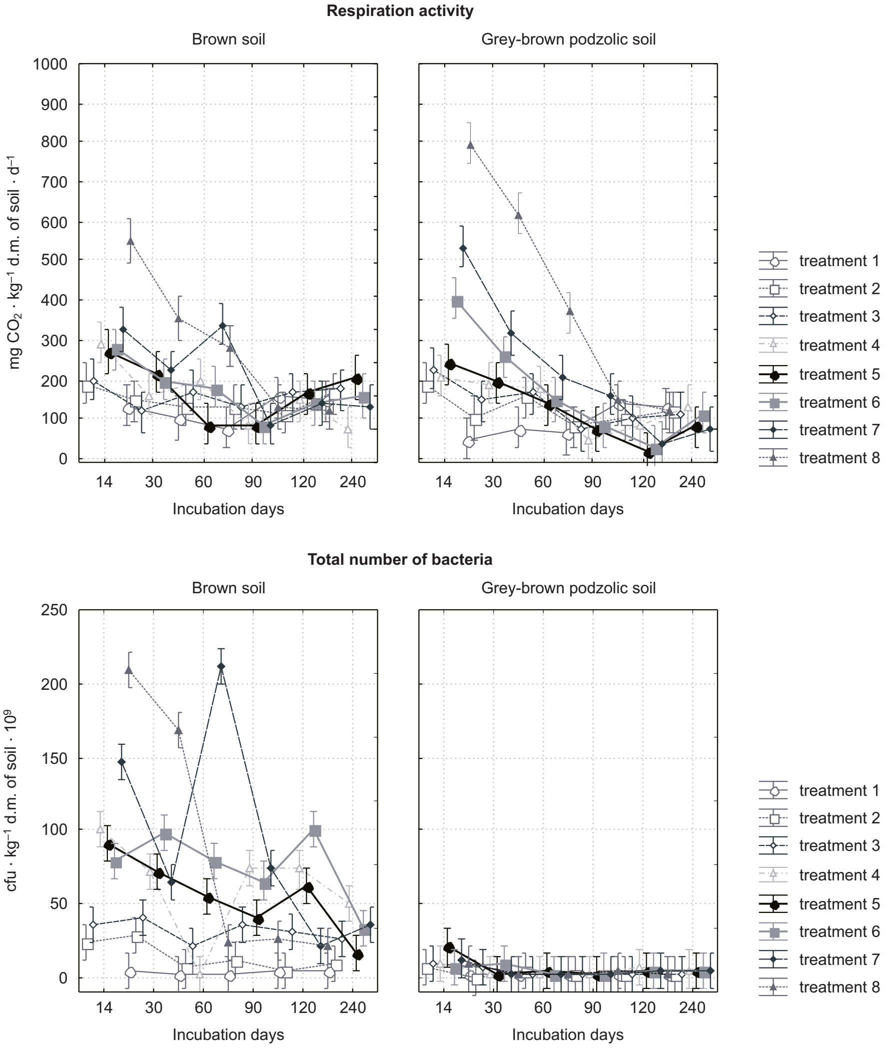

Fig. 1. Respiration activity and numbers of bacteria depending on dairy sewage sludge addition
Explanations: Treatments per 1 kg of soil: 1 – control soil, without fertilisation; 2 – 10 g of dairy sewage sludge; 3 – 20 g of dairy sewage sludge; 4 – 26.7 g of dairy sewage sludge; 5 – 40 g of dairy sewage sludge; 6 – 66.7 g of dairy sewage sludge; 7 – 100 g · kg^{-1} of dairy sewage sludge; 8 – 200 g of dairy sewage sludge

significantly with increasing doses of sludge introduced in the soil. Beginning from the 30th day of incubation there occurred a rapid decrease in the numbers of the studied microorganisms, attaining the minimum level on 90ties day of the experiment, after which the numbers of that group of bacteria increased again.

Significantly higher numbers of proteolytic bacteria were found in the grey-brown podzolic soil than of the brown soil. The numbers of fungi with proteolytic capabilities

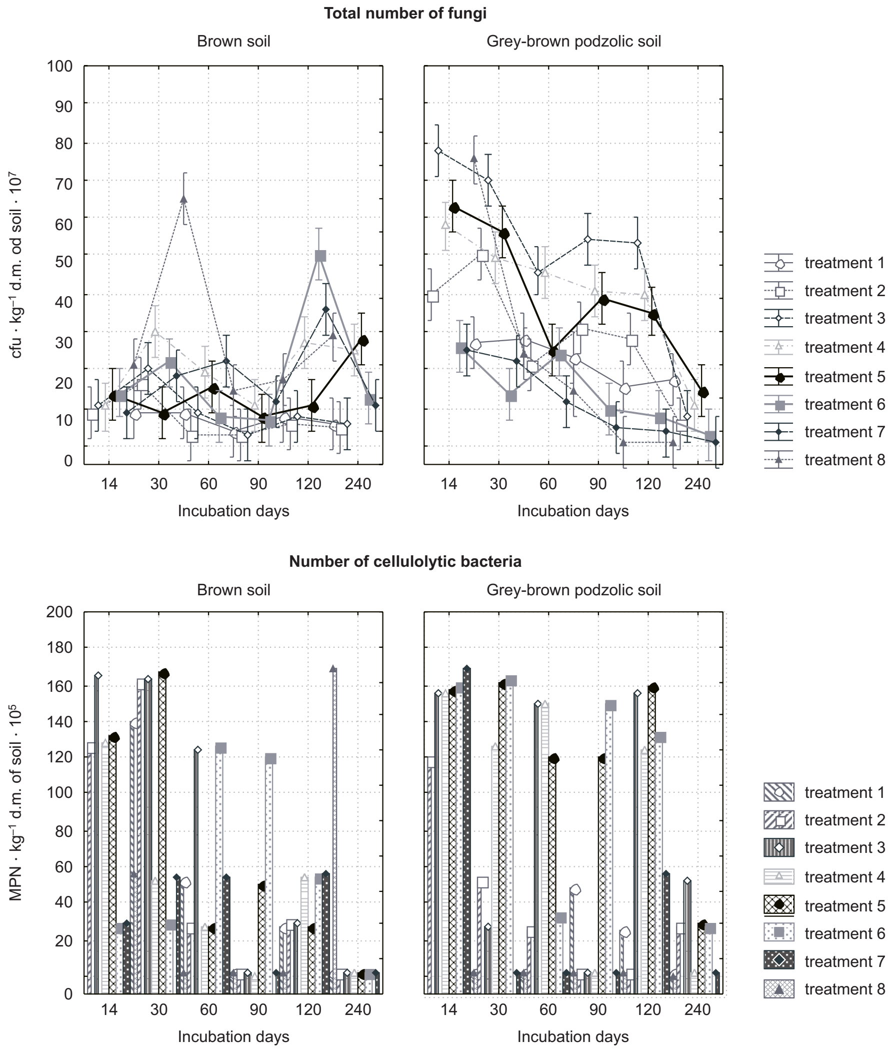

Fig. 2. Numbers of fungi and celulolytic bacteria depending on dairy sewage sludge addition
Explanations: See Fig. 1

in the soils amended with varied doses of dairy sewage sludge were subjected to periodic variation (Fig. 3). All of the applied sludge doses caused stimulation of the growth of the studied group of fungi and the highest numbers being characteristic of treatments with the highest dose of the sludge, ie 200 g · kg^{-1}. A significantly greater number of proteolytic fungi was found in the grey-brown podzolic soil compared with the brown soil.

Periodic changes in the numbers of ammonising bacteria in the individual experimental treatments for both soils studied are presented in Fig. 4. The results of the

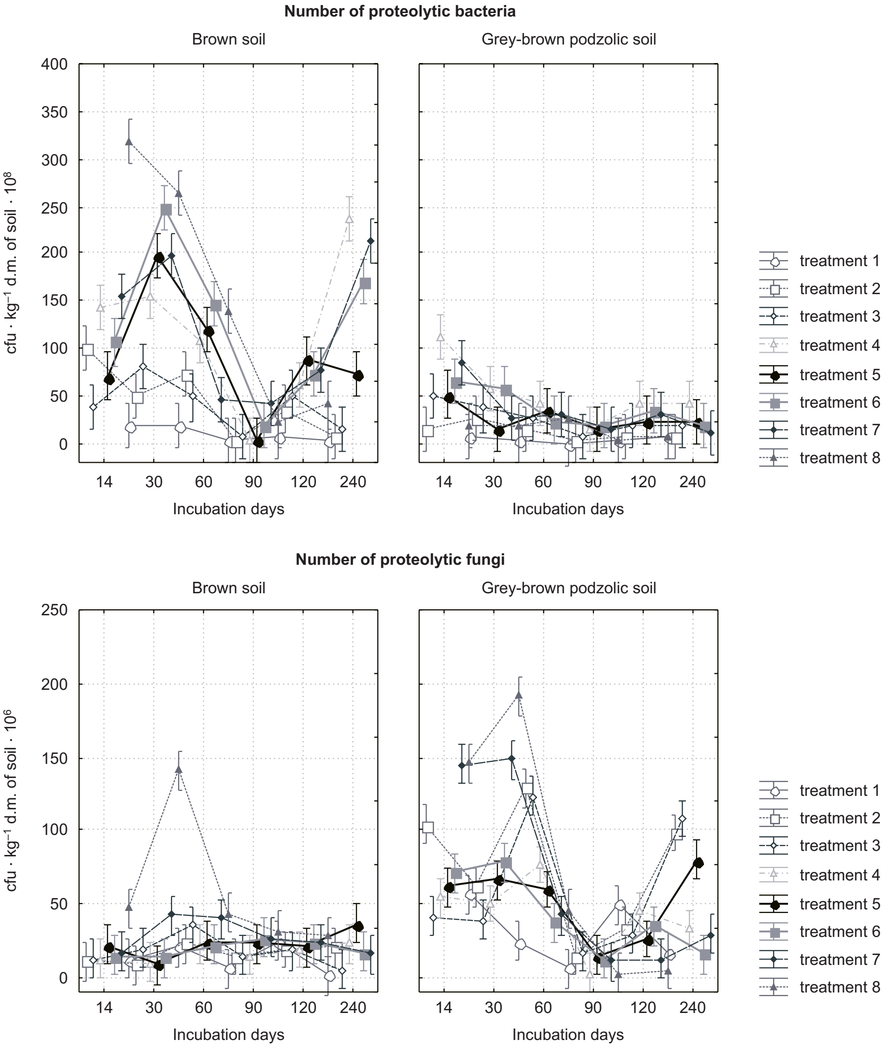

Fig. 3. Numbers of proteolytic bacteria and fungi depending on dairy sewage sludge addition
Explanations: See Fig. 1

analyses indicate that the growth of that microbial group was related to the applied dose of the sludge and increased with increasing amounts of sludge introduced into the soil.

The numbers of ammonisers, as those of most of the studied microbial groups, tended to decrease with the progressing duration of the experiment. A higher mean number of ammonising bacteria was observed in the grey-brown podzolic soil than in the brown soil. Notable periodic variation was observed in the numbers of nitrifying bacteria, as presented in Fig. 4. Analysis of results revealed an increase in the numbers of those bacteria with increasing doses of the sludge introduced in the soil, the highest

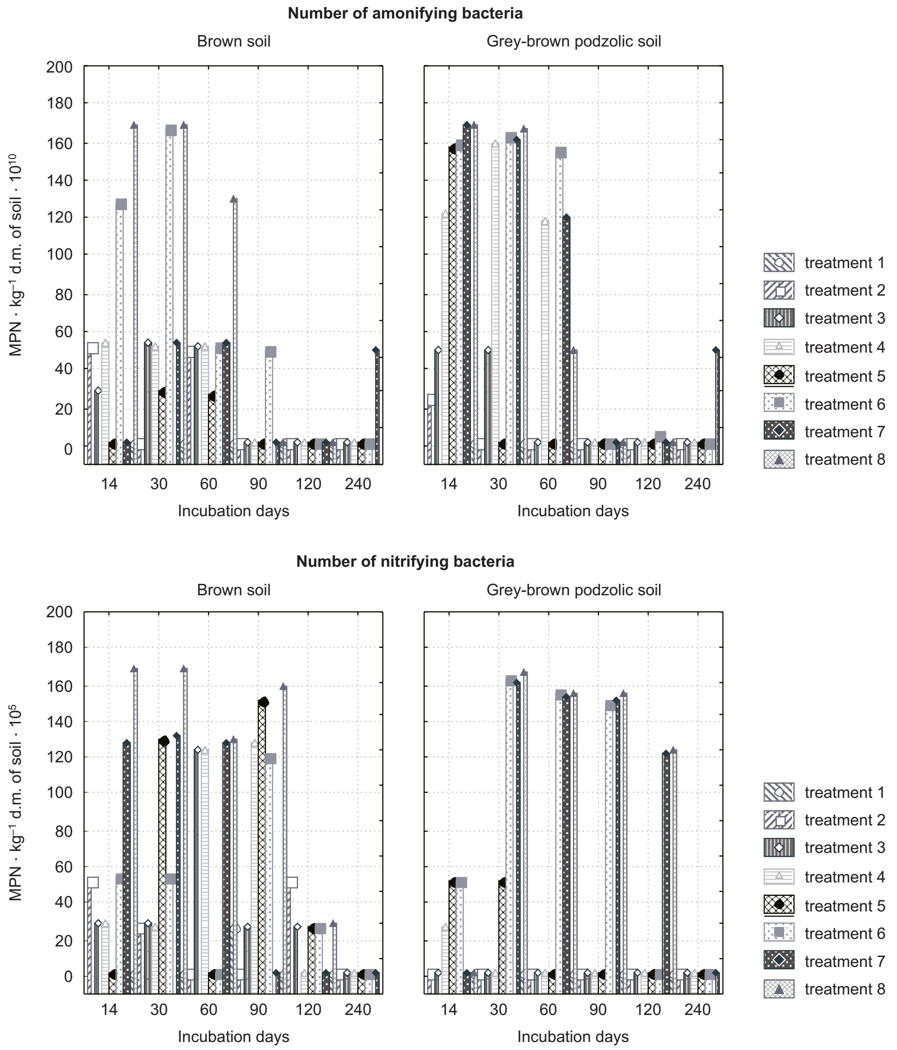

Fig. 4. Numbers of amonifying bacteria and nitryfying bacteria depending on dairy sewage sludge addition
Explanations: See Fig. 1

number of nitrifying bacteria being characteristic of the treatments with the highest dose of the sludge, ie 200 g · kg^{-1}. A higher number of nitrifying bacteria was found in the brown soil.

Discussion

The numbers of the particular physiological groups are employed as a microbiological parameter permitting the estimation of the quantitative composition of microorganisms participating in the decomposition of specific organic compounds [15]. For this reason determination of the number of various microbial groups is frequently used for the determination of the biological condition of the soil environment, especially in soils subjected to the effect of anthropogenic factors [16–19].

The study reported herein showed that the numbers of microorganisms in the studied soils were significantly dependent on the experimental factors applied, ie the fertiliser introduced in the soil, time of its action, as well as the type of soil. The results of the study showed a stimulating effect of the dairy sewage sludge with relation to the studied microbial groups. The effect is probably related with the introduction of organic matter and mineral components into the soil, those being nutritional substrates for the particular groups of soil microorganisms. Stimulation of microbial growth in soils fertilised with sewage sludge was also observed by other authors [16, 19–21]. This study showed that the number of bacteria and fungi increased significantly with increasing doses of the sludge introduced in the soil, which should be attributed to the accumulation of nutrients introduced into the soil with the higher doses of the waste. Lima et al [22] also observed stimulation of the growth of bacteria and fungi under the effect of fertilisation with municipal sewage sludge, which was intensified with increasing doses of sludge introduced in the soil. Stimulation of the growth of fungi should be attributed to increase in the content of organic carbon after the introduction of the sludge, and to low pH value of the grey-brown podzolic soil. Hence in this study greater number of fungi was characteristic of the grey-brown podzolic soil amended with the sludge than the brown soil. Bacterial growth became more noticeable in the brown soil, with reaction close to the neutral, as those microorganisms prefer such environments. The significantly higher numbers of bacteria and fungi at the initial stage of the experiment could have been related with the growth of microbial groups mineralising easily available organic mater. In the study the so-called total number of bacteria, and the number of "proteolytic", ammonising and nitrifying bacteria and fungi were the highest in the treatments with the sludge dose of 200 $g \cdot kg^{-1}$. A positive effect of fertilisation with dairy sewage sludge on the numbers of soil bacteria and fungi was also demonstrated in an earlier study by Jezierska-Tys and Frąc [23]. Culturing of both microbial groups under study usually involved an increase in the respiratory activity which, according to some authors [3, 15, 24], is a measure of the overall microbiological activity of soils. The study showed also stimulation of the growth of cellulolytic bacteria in soils fertilised with dairy sewage sludge. Particularly intensive growth of that microbial group was observed in the grey-brown podzolic soil. A study by Furczak and Joniec [25] also showed an increase in the number of cellulolytic bacteria in a soil fertilised with municipal sewage sludge.

Introducing into soil dairy sewage sludge which is a source of various nitrogen complexes, beginning with organic nitrogen compounds through a series of mineral forms [8], had a significant effect on the population size of microorganisms involved in nitrogen transformations in the soil. The study reported herein demonstrated a stimulating effect of the sludge on the growth of "proteolytic" bacteria and fungi. That effect was caused by organic compounds introduced in the soil with the sludge, those compounds being a substrate for those microbial groups. Another factor conducive to the growth of proteolytic bacteria in particular could have been increase in the soil reaction. Noteworthy is the fact that the numbers of the microorganisms under study increased in the soil together with increasing doses of the sludge applied. Determinations of the numbers of proteolytic bacteria and fungi show that their growth was related both to the dose of the diary sewage sludge and to the soil type. Greater numbers of proteolytic bacteria were observed in the brown soil compared with the grey-brown podzolic soil, while in the case of fungi with the capability of decomposing organic nitrogen complexes an inverse tendency was noted. The population sizes of the studied microbial groups increased with increasing doses of the sludge introduced in the soil, the effect – in the case of bacteria – being more pronounced in the brown soil, and in the case of fungi – in the grey-brown podzolic soil. This phenomenon may be attributed to the introduction in the soil of a substrate necessary for the growth of those microorganisms, in the form of organic nitrogen compounds present in the dairy sewage sludge. As reported by Fidecki [26], nitrogen occurs in such wastes mainly in the organic form, and its mineralisation takes place with participation of proteolytic microorganisms. A stimulating effect of municipal sewage sludge on the growth of proteolytic bacteria was also observed in their studies by Joniec and Furczak [27] and by Jezierska-Tys and Frac [23]. The study reported herein also demonstrated a stimulating effect of dairy sewage sludge on the number of ammonising and nitrifying bacteria, intensifying with increase in the dosage of the sludge introduced in the soil. That effect may indicate soil properties favourable for plants, as those microbial groups, especially nitrifiers, are sensitive to soil acidification and insufficient aeration [28]. The presence of those microbial groups is of key importance in making nitrogen available to plants. The decrease in the numbers of the studied microorganisms in the course of the experiment indicates depletion of the nutritional substrates for those microbial groups.

Conclusions

1. The study demonstrated that soil amendment with diary sewage sludge had a significant effect on the populations of soil microorganisms.
2. The effect of the sludge on the microbial groups under study depended on the dose of the sludge, on the type of soil, and on the kind of microbiological parameter.
3. It was demonstrated that the dairy sewage sludge stimulated the growth of microorganisms in the soil environment. The effect intensified with increasing dosage of the sludge introduced in the soil.
4. A significant relationship was demonstrated between the respiratory activity and the growth of microorganisms in soil fertilised with dairy sewage sludge.

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ZMIANY AKTYWNOŚCI MIKROBIOLOGICZNEJ GLEB NAWOŻONYCH ZRÓŻNICOWANYMI DAWKAMI OSADU Z OCZYSZCZALNI ŚCIEKÓW MLECZARSKICH

[1] Zakład Badań Systemu Gleba–Roślina
Instytut Agrofizyki im. B. Dobrzańskiego Polskiej Akademii Nauk w Lublinie
Katedra Mikrobiologii Rolniczej
[2] Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Celem przeprowadzonych badań była ocena wpływu zróżnicowanych dawek osadu ścieków mleczarskich na kształtowanie się liczebności wybranych grup drobnoustrojów i aktywności respiracyjnej w glebie brunatnej i płowej. Modelowe badania laboratoryjne przeprowadzono na dwóch różnych typach gleb (brunatnej i płowej). Analizy mikrobiologiczne wykonywane okresowo w czasie trwania doświadczenia obejmowały oznaczenie aktywności respiracyjnej i liczebności wybranych grup mikroorganizmów glebowych. Oddziaływanie osadu z oczyszczalni ścieków mleczarskich na badane grupy drobnoustrojów zależało od ilości dawki odpadu, typu gleby oraz rodzaju parametru mikrobiologicznego.

Słowa kluczowe: aktywność respiracyjna, gleba, mikroorganizmy, osad ścieków mleczarskich

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Krzysztof GONDEK[1] and Barbara FILIPEK-MAZUR[1]

YIELDING AND THE CONTENTS OF CALCIUM, MAGNESIUM AND SODIUM IN MAIZE FERTILIZED WITH ORGANIC MATERIALS

PLONOWANIE ORAZ ZAWARTOŚĆ WAPNIA, MAGNEZU I SODU W KUKURYDZY NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI

Abstract: The use of sewage sludge for plant fertilization seems to be the most rational method of their management, which does not imply their advantageous effect on the yield biological value. Because of the necessity of balancing minerals in animal nutrition, the investigations aimed at an assessment of the contents of calcium, magnesium and sodium in maize biomass fertilized with sewage sludge and mixtures sewage sludge and peat, cultivated in soils with diversified texture. Over the three year period of the experiment, fertilization with sewage sludge and sludge mixtures with peat, had a more favourable effect on maize biomass yield than treatment with mineral salts.

Maize fertilization with sewage sludge and sludge mixtures with peat did not cause any significant increase in the contents of the analyzed macroelements, except for calcium in maize shoots, in comparison with farmyard manure. Fodder value of the obtained maize shoots was low with respect to the investigated elements. Low value of Ca:Mg ratio evidences that the analyzed maize biomass contained too small amounts of calcium in relation to magnesium. While using the plant biomass fertilized with sewage sludge or other waste materials for animal feeds, one should remember about supplementing mineral components, such as Ca, Mg and Na because the amounts of these elements taken up by animals may be insufficient.

Keywords: calcium, magnesium, sodium, maize, sewage sludge

Fertilization is a factor, which among the cultivation measures, such as tillage, crop rotation or application of plant protection chemicals, most strongly affects plant chemical composition. It is difficult to assess fertilization effect on crop quality because of the proper selection of quality indices, whereas the comparison of nutritional results and an assessment based on the chemical composition of the forage fed to animals are not always fully compatible [1].

Plant fertilization with waste materials, including sewage sludges may play an important role in supplying them with mineral components such as: calcium, magnesium or sodium. These elements are crucial for animal nutrition and fulfill various physical, chemical or biological functions in their organisms. Their occurrence in animal organism depends mainly on feed abundance in these elements and their bioavailability [2].

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[1] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone 12 662 4346, fax +48 12 662 4341, email: rrgondek@cyf-kr.edu.pl

The use of sewage sludge for plant fertilization seems to be the most rational way of their utilization, which however does not imply their beneficial effect on biological value of yield. Because of the necessity of balancing the quantity of mineral components in animal nutrition, the research aimed at an assessment of the contents of calcium, magnesium and sodium in biomass of maize fertilized with sewage sludge and mixtures sewage sludge and peat cultivated in soils with diversified texture.

Materials and methods

The assessment of fertilization effect on the contents of calcium, magnesium and sodium in maize biomass was conducted in a two-factor pot experiment (factors: soil and fertilization) in 2003–2005. The investigations were carried out on three soils and the experimental design was the same for each soil. It comprised the following treatments (in four replications on each soil): unfertilized (0); mineral treatment (NPK); farmyard manure – (OB); sewage sludge A (OŚA); mixture of sewage sludge A and peat – (MOŚA); sewage sludge B (OŚB) and a mixture of sewage sludge B and peat (MOŚB). The following soil material was used for the experiment: weakly loamy sand (psg), sandy silt loam (gpp) and medium silt loam (gśp), which were collected from the arable layer (0–20 cm) of ploughlands near Krakow. Sewage sludge obtained from two different mechanical-biological municipal treatment plants and their mixtures with peat were used for the experiment (sewage sludge were mixed with peat in weight ratio 1 : 1 per dry mass of organic materials). Peat with dry mass content 408 $g \cdot kg^{-1}$ contained: 88 $g \cdot kg^{-1}$ ash; 13.6 $g\ Ca \cdot kg^{-1}$ d.m.; 0.74 $g\ Mg \cdot kg^{-1}$ d.m. and 0.16 $g\ Na \cdot kg^{-1}$ d.m. The characteristics of chemical composition of the organic materials and soil material (values per dry mass assessed at 105 ^{o}C) were given in Tables 1 and 2.

PVC pots used for the experiment contained 5.50 kg of air-dried soil material. Before the experiment outset the soils were gradually moistened to 30 % of maximum water capacity. After moistening sandy silt loam and medium silt loam were limed to obtain the soil pH required by the decree [3]. The measure was applied separately in each pot. Chemically pure CaO was used in a dose calculated on the basis of soil hydrolytic acidity. Subsequently all soils were left for 4 weeks and water loses were supplemented occasionally. After this period organic materials were introduced in the amount corresponding to 1.20 $g\ N \cdot pot^{-1}$. Phosphorus and potassium quantities introduced to the soil with organic materials were equalized with solutions of chemically pure salts [$Ca(H_2PO_4)_2 \cdot H_2O$ and KCl]. On mineral (NPK) treatment the identical nitrogen, phosphorus and potassium doses were used as on the organic material treatments, respectively: 1.20 $g\ N \cdot pot^{-1}$ as NH_4NO_3, 1.26 $g\ P \cdot pot^{-1}$ as $Ca(H_2PO_4)_2 \cdot H_2O$ and 1.48 $g\ K \cdot pot^{-1}$ as water solution of KCl. Considering the consequent fertilizer effect and the soils' abundance in bioavailable phosphorus and potassium, in the second and third year of the experiment, the following doses of fertilizer components were applied: 0.80 g N; 0.2 g P and 1.40 $g\ K \cdot pot^{-1} \cdot year^{-1}$ as solutions of chemically pure salts.

Maize, 'San' c.v. (FAO 240), was cultivated as a test plant each year and 5 pieces per pot were left. Maize (for green forage) was harvested at the 7–9 leaves stage. Growing periods were respectively: 47 days in the first year, 66 days in the second and 54 days in the third one. Throughout the experiment the plants were watered with distilled water to

50 % of maximum water capacity. After the harvest the plants were dried (at 70 °C) to constant weight and the yield of dry mass of shoots and roots was determined. Dried biomass was crushed in a laboratory mill and mineralized in a muffle furnace (at 450 °C for 5 hours). The remains were dissolved in diluted nitric(V) acid 1 : 2 (v/v) [4]. In the obtained plant material solutions, calcium and sodium were determined with flame photometry method (FES) and magnesium with atomic absorption spectrometry (AAS) on Philips PU 9100X apparatus. Plant reference material NCS DC73348 (China National Analysis Center for Iron & Steel) and soil reference material *Agro*MAT AG-2 (SCP Science) was attached to each analytical series. The results were verified statistically using a fixed model (factors: fertilization, soil). The statistical computations considered one-way or two-way ANOVA and the significance of differences was estimated using LSD Fisher test at significance level $p < 0.05$ [5].

Results and discussion

The organic materials applied in the experiment differed with their chemical composition including calcium, magnesium and sodium content. Calcium content in sewage sludge was higher than assessed in farmyard manure, whereas the quantities of magnesium and sodium were smaller (Table 1).

Table 1

Chemical composition of materials used in experiment

Determination		FYM (OB)	Sewage sludge (OŚA)	Sewage sludge + peat (MOŚA)	Sewage sludge (OŚB)	Sewage sludge + peat (MOŚB)
Dry matter $[g \cdot kg^{-1}]$		189	310	343	418	372
pH (H_2O)		6.22	6.12	5.57	5.73	5.20
Organic matter $[g \cdot kg^{-1}$ d.m.]		679	353	652	552	771
Total content						
N	$[g \cdot kg^{-1}$ d.m.]	21.6	17.0	24.7	37.4	35.1
S		7.24	8.81	6.23	14.62	7.85
P		22.60	5.48	3.00	19.32	7.64
K		26.69	2.71	1.88	2.81	1.64
Ca		4.83	15.66	13.31	9.22	11.95
Mg		6.26	4.86	2.82	2.55	1.59
Na		4.60	0.54	0.40	0.70	0.44
Cr	$[mg \cdot kg^{-1}$ d.m.]	6.07	19.74	10.25	37.88	17.47
Zn		531	899	488	1684	821
Pb		3.99	65.9	38.2	29.4	17.5
Cu		338	78.3	40.6	119.4	51.8
Cd		1.28	2.71	1.45	2.25	1.03
Ni		11.74	13.32	7.14	25.36	12.07
Hg		trace	3.58	1.80	2.29	1.07
Mn		379	129	102	277	163

Peat supplement to the sludge generally diminished the contents of most elements in the mixture in comparison with their contents in the sludge, except for calcium content in sewage sludge B mixture (MOŚB), which resulted from higher content of this element in peat.

The soil material used for the experiment belonged to various texture groups but also significantly differed with chemical properties (Table 2).

Table 2

Some properties of soils before the establishment of the experiment

Determination			Soil		
			(psg)	(gpp)	(gśp)
Granulometric composition ∅	1.0–0.1 mm	[%]	78	42	28
	0.1–0.02 mm		13	33	29
	< 0.02 mm		9	25	43
pH KCl			6.21	5.69	5.30
Hydrolitic acidity		[mmol(+) · kg^{-1} d.m.]	11.2	23.4	33.2
Sum of alkaline cation			39.9	86.8	128.4
Total N		[g · kg^{-1} d.m.]	0.96	1.25	1.72
Organic C			9.37	13.36	17.68
Total S			0.16	0.28	0.32
Available forms					
P		[mg · kg^{-1} d.m.]	79	217	29
K			166	359	138
Mg			134	154	126
S-SO$_4$			13.4	11.9	11.4

Analysis of variance confirmed a significant effect of fertilization with organic materials on maize biomass yield (Fig. 1).

Treatment with sewage sludge or their mixtures with peat and farmyard manure fertilization allowed to obtain significantly greater yields than gathered on treatments fertilized exclusively with mineral compounds. In case of sewage sludge mixture with peat application (except for MOŚA mixture on sandy silt loam) larger yields were produced than when solely sewage sludge was used. This result cannot be fully ascribed to the consequent fertilizer effect of sewage sludge or their mixtures with peat. Supplementary fertilization with mineral salts in the second and third year of the experiment also had a significant influence on the biomass yield. Supplying to the soil with organic materials components such as sulphur, magnesium or microelements, whose quantities were not balanced, might have been also the factor determining maize yielding. Application of natural or organic fertilizers not always leads to an increase in crop yields in result of the consequent effect. Wiater et al [6] obtained worse direct effect of sewage sludge granulate on maize yield in comparison with mineral fertilization, but the consequent fertilizer effect of sewage sludge was better. Drab and Derengowska [7] proved a positive influence of sewage sludge fertilization on crop yields and at the same time demonstrated that the amount of plant yields, irrespective of the soil was also conditioned by sewage sludge dose.

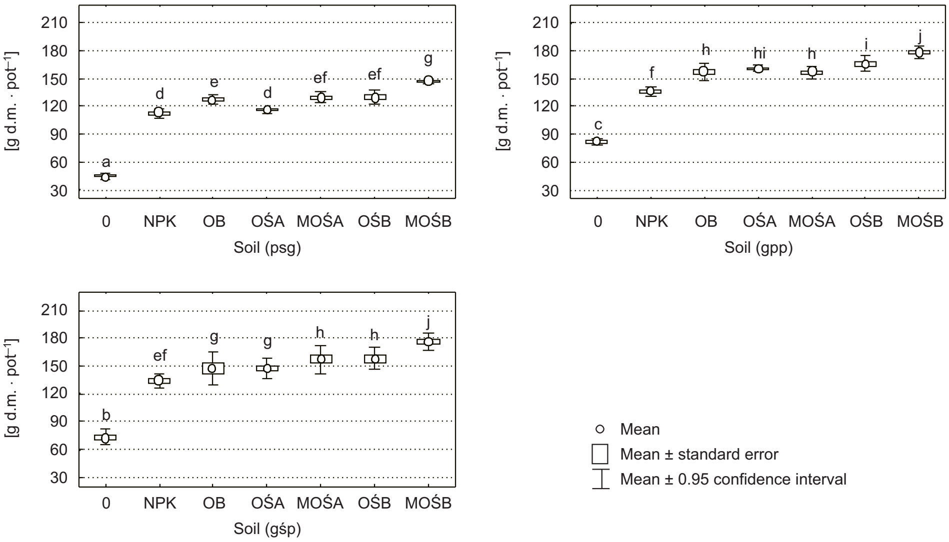

Fig. 1. Yield of aboveground parts of maize (sum of dry matter from three years)
Means followed by the same letters did not differ significantly at $p < 0.05$ according to the Fisher test

Disturbed relationships between nutrients, particularly when their quantity supplied with fertilization is not balanced, may affect plant mineral economy and condition biological value of the produced yield.

Indispensability of calcium in animal feeds results in the first place from the key role this element plays in bone formation process. Moreover, it is crucial for proper functioning of muscle and nervous system, the heart, cell membrane permeability and blood coagulation [2]. Calcium contents in maize biomass were diversified depending mainly on the plant part (Table 3).

Table 3

3-year period weighted average content of macroelements
in aboveground parts and roots of maize (for soils)

Object	Ca		Mg		Na	
	[g · kg^{-1} d.m.]					
	Cz.n.	K	Cz.n.	K	Cz.n.	K
Control (0)	1.52d	2.18a	2.53b	1.94a	0.23a	1.10b
NPK (NPK)	1.23bc	6.38e	1.85a	2.78b	0.26a	0.72a
FYM (OB)	0.96a	3.25ab	1.63a	2.24ab	0.31b	1.99c
Sewage sludge (OŚA)	1.36cd	5.99de	1.88a	2.55ab	0.33b	0.81a
Sewage sludge + peat (MOŚA)	1.25bc	4.89cd	1.83a	2.31ab	0.27ab	0.75a
Sewage sludge (OŚB)	1.32bcd	4.62c	1.97a	2.45ab	0.33b	0.78a
Sewage sludge + peat (MOŚB)	1.12b	3.94bc	1.70a	2.25ab	0.28ab	0.70a

Cz.n. – aboveground parts; K – roots; Means followed by the same letters in columns did not differ significantly at $p < 0.05$ according to the Fisher test.

Greater amounts of this element were detected in maize biomass with no fodder value, ie in roots. Maize fertilizing with sewage sludge and mixtures of sewage sludge with peat affected calcium content in the plant shoots more than farmyard manure treatment (Fig. 2).

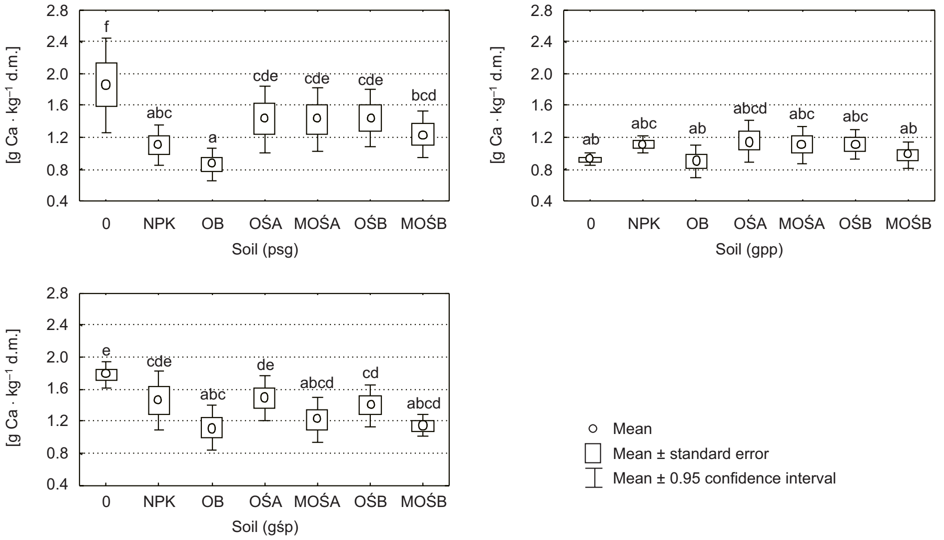

Fig. 2. Weighted average content of calcium in aboveground part of maize (from three years)
Means followed by the same letters did not differ significantly at $p < 0.05$ according to the Fisher test, factors soil x fertilisation

No significant diversification in calcium content was found in maize shoots cultivated in individual soils, excepts the unfertilized treatments. Woloszyk [8] found that one should not expect increasing calcium content in plants fertilized with organic materials either as a consequent effect or in result of a greater dose. On the other hand Lekan and Winiarska [9] think that plants fertilized with sewage sludge may accumulate considerable quantities of among others calcium, which should be associated with a substantial amount of this element in sewage sludge. In their previous investigations Gondek and Filipek-Mazur [10] proved that application of sewage sludge for plant fertilization significantly increased their calcium contents. However, it should be mentioned that the applied sewage sludge contained much bigger amounts of this element. Estimation of maize shoot biomass with respect to calcium content, revealed a low calcium content from the perspective of maize destination for fodder [11].

Magnesium content is important for plant fodder utility. In animal organism magnesium is the element constructing the skeleton and together with potassium is the most important mineral component of cell, and additionally also activator of many enzymes [2]. Maize root system contained greater amounts of magnesium (similar as calcium) than the shoots (Table 3). Although maize roots system has no fodder value, its magnesium content can signalize the quantity of this element which may be released in result of harvest residue mineralization and provide a source of this element for the consecutive plant. On the basis of the obtained results it was found that the applied fertilization did not diversify magnesium contents in maize tops (Fig. 3).

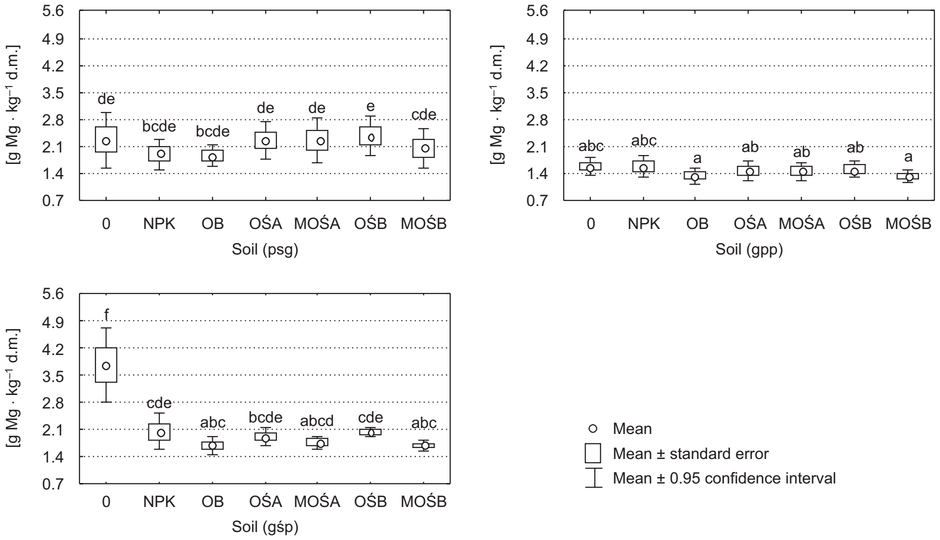

Fig. 3. Weighted average content of magnesium in aboveground part of maize (from three years) Means followed by the same letters did not differ significantly at $p < 0.05$ according to the Fisher test, factors soil x fertilisation

However, magnesium content in maize shoots was markedly diversified depending on the kind of soil. The smallest amounts of this element were detected in maize shoots cultivated in sandy silt loam (gpp). Lekan and Winiarska [10] also assessed comparable contents of magnesium in plants fertilized with industrial-municipal sewage sludge and industrial sludge. As results from the quoted investigations there is no unanimous opinion on the influence of fertilization, particularly with organic materials, on macroelement contents in plant biomass. It may be due to a considerable variability of properties of organic materials used for the treatment, but mainly by the degree of their processing if they are waste materials. In the earlier Authors' investigations a relatively difficult access to nutrients from the applied organic materials might have actually limit magnesium uptake by plants. The analysis of magnesium contents in maize shoots in view of fodder value revealed its very low content, except its content in biomass of plant cultivated in weakly loamy sand (psg) fertilized with sewage sludge and mixtures of sewage sludge and peat [11].

Plant sodium requirement is small. Its functions comprise primarily effects on physicochemical soil properties and water economy in plants. Sodium content in plants has been considered mainly with respect to animal nutritional needs to which this element is necessary in considerably larger amounts. Sodium in animal organism is present almost exclusively in ionized form, mainly in extracellular liquids [2]. Sodium content in maize shoots fertilized with organic materials (sewage sludge, mixtures of sludge and peat) was over twice smaller than assessed in plant roots (Table 3). For comparison, shoots of maize fertilized with farmyard manure contained over 6 times less sodium than the roots. The applied fertilization diversified sodium content mostly in maize shoots cultivated in weakly loamy sand (psg) (Fig. 4).

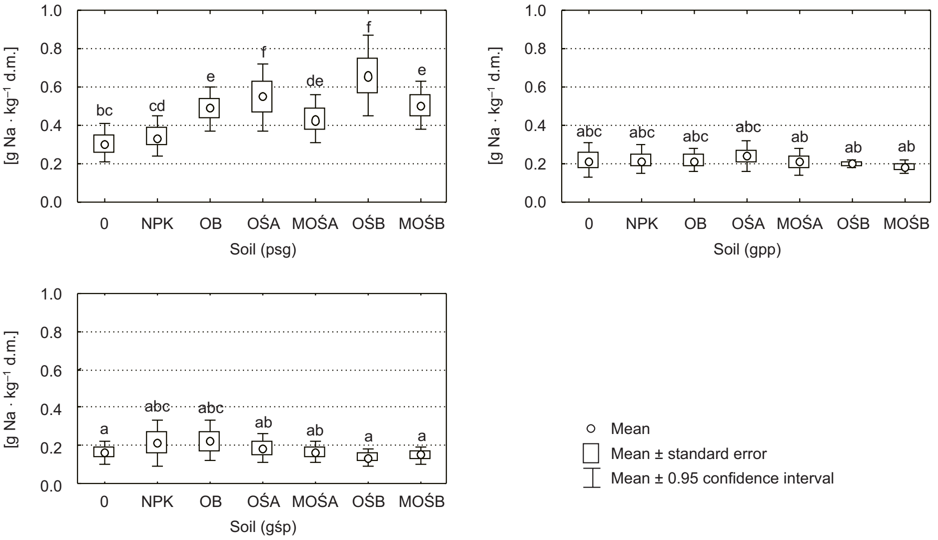

Fig. 4. Weighted average content of sodium in aboveground part of maize (from three years) Means followed by the same letters did not differ significantly at $p < 0.05$ according to the Fisher test, factors soil x fertilisation

Significantly greatest amounts of this element were registered in the biomass of plants fertilized with sewage sludges. Sodium content in shoots of maize cultivated in sandy silt loam (gpp) and in medium silt loam differed significantly, irrespective of the applied fertilization. In previous investigations conducted by Gondek and Filipek-Mazur [10] no major changes were noted in sodium content in biomass of plants fertilized with sewage sludge. Sodium contents determined in the plant yield were comparable with the quantities assessed in the plants receiving mineral salts. Kopec et al [12] found greater sodium contents in the plants fertilized with sewage sludge but originating from tanneries with much higher content of Na. Studies of Mazur and Koc [10] revealed that plant fertilization with tannery sludge particularly affects sodium contents because of high concentration of this element, but does not influence calcium or magnesium contents. Considering fodder value, sodium content in maize shoots was low [11].

Quantitative relationships between nutrients are a good indicator of feed quality. According to Czuba and Mazur [14] one of such indicators is Ca : Mg ratio, which should equal 3 : 1. In the presented Authors' own investigations mean value of this ratio was the smallest, irrespective of the soil, in maize shoots fertilized with farmyard manure (Fig. 5).

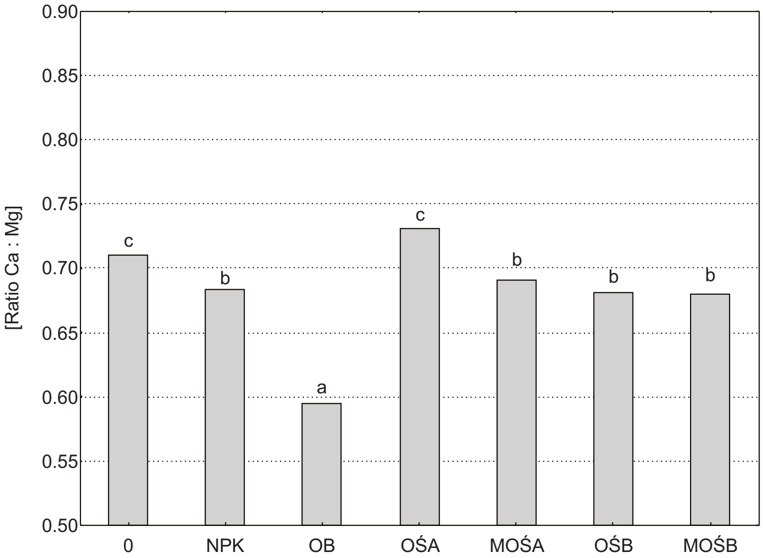

Fig. 5. Mean (for year and soils) value of the weight ratio Ca : Mg in aboveground part of maize Means followed by the same letters did not differ significantly at $p < 0.05$ according to the Fisher test, factors soil x fertilisation

Ca : Mg value in the biomass maize shoots fertilized with sewage sludge and their mixtures with peat did not exceed the value of 0.75. The highest value of Ca : Mg ratio was registered in maize shoots fertilized with sewage sludge A (OŚA). Low value of Ca : Mg ratio testifies the fact that the analyzed maize shoot biomass contained too small quantities of calcium in comparison with magnesium.

Conclusions

1. Fertilization with sewage sludge and mixtures of sewage sludge with peat, applied over the three years of the experiment, had a more advantageous effect on maize biomass yield than treatment with mineral salts.
2. Maize fertilization with sewage sludge and mixtures of sewage sludge and peat did not cause any significant increase in the analyzed macroelements, except calcium, in maize shoots in comparison with farmyard manure treatment.
3. Fodder value of the maize shoot biomass was low in respect of the content of the analyzed elements.
4. Low value of Ca : Mg ratio evidences that the analyzed maize biomass contained too little calcium in relation to magnesium.
5. When using biomass of plants fertilized with sewage sludge or other waste materials for fodder purposes one should remember about supplementing mineral components such as Ca, Mg and Na because the quantity of these components absorbed by animals with fodder may prove insufficient.

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PLONOWANIE ORAZ ZAWARTOŚĆ WAPNIA, MAGNEZU I SODU W KUKURYDZY NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy w Krakowie

Abstrakt: Wykorzystanie osadów ściekowych do nawożenia roślin wydaje się najbardziej racjonalnym sposobem ich utylizacji, co nie jest równoznaczne z ich korzystnym działaniem na wartość biologiczną plonu. Wobec konieczności bilansowania ilości składników mineralnych w żywieniu zwierząt, celem przeprowadzonych badań była ocena zawartości wapnia, magnezu i sodu w biomasie kukurydzy nawożonej osadami ściekowymi i mieszaninami osadów ściekowych z tordem, uprawianej na glebach o zróżnicowanym składzie granulometrycznym.

Nawożenie osadami ściekowymi i mieszaninami osadów ściekowych z torfem w trzyletnim okresie badań działało korzystniej na plon biomasy kukurydzy niż nawożenie solami mineralnymi. Nawożenie kukurydzy osadami ściekowymi i mieszaninami osadów ściekowych z torfem nie spowodowało znacznego zwiększenia zawartości badanych makroskładników, poza wapniem w częściach nadziemnych kukurydzy, w porównaniu z nawożeniem obornikiem. Wartość paszowa uzyskanej biomasy części nadziemnych kukurydzy pod względem zawartości badanych pierwiastków była mała. Mała wartość stosunku Ca : Mg świadczy, że analizowana biomasa kukurydzy zawierała za mało wapnia w stosunku do magnezu. Przy wykorzystaniu biomasy roślin nawożonych osadami ściekowymi lub innymi materiałami pochodzenia odpadowego do celów paszowych należy pamiętać o uzupełnieniu składników mineralnych, takich jak Ca, Mg i Na, ponieważ ilość tych składników pobrana przez zwierzęta z paszą może okazać się niewystarczająca.

Słowa kluczowe: wapń, magnez, sód, kukurydza, osady ściekowe

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Katarzyna IGNATOWICZ[1]

ASSESSMENT USABILITY OF JERUSALEM ARTICHOKE (*Helianthus tuberosus* L.) FOR PHYTOREMEDIATION OF SOIL CONTAMINATED WITH PESTICIDES

OCENA PRZYDATNOŚCI TOPINAMBURU (*Helianthus tuberosus* L.) DO FITOREMEDIACJI GLEBY ZANIECZYSZCZONEJ PESTYCYDAMI

Abstract: The aim of present research was to assess the usefulness of Jerusalem artichoke (*Helianthus tuberosus* L.) to phytoremediation of sorption substrate contaminated with pesticides. Studies upon purification of sorption substrate consisting of a soil and dairy sewage sludge were conducted under pot experiment conditions. The study design included control pot along with 3 other ones polluted with pesticides. The vegetation season has lasted since spring till late autumn 2007. After plants acclimatization, the mixture of chloro- and phosphoorganic pesticides was added into 3 experimental pots in the continuous intervals. After harvest the samples of substrate and plant material, both tops and roots, were taken. It was found that pesticide contents in sorption subsoil (from 0.10313 to 0.38909 mg $\cdot$ kg^{-1} d.m.) were much higher than in control soil (from 0.01781 to 0.22702 mg $\cdot$ kg^{-1} d.m.). Achieved results allow initially certify that Jerusalem artichoke can be used for reclamation of soils contaminated with pesticides, particularly for vitality prolongation of sorption barrier around the graveyard area. In future, it would allow for applying the sorption screen around pesticide graveyard, which reduces pesticide migration into the environment, and grown energetic plants – through phytoremediation – would prolong the sorbent vitality and remove pesticides from aboveground parts by means of combustion.

Keywords: phytoremediation, Jerusalem artichoke (*Helianthus tuberosus* L.), sorption, pesticide, graveyard

Waste dumps with outdated and useless plant protection means are the most serious threat for natural environment, the use of agrichemicals could cause in Poland. In the case of corrosion and damage of pesticide graveyard site construction, a continuous supply of contaminants to open waters occurs and will occur for many years [1–3]. Therefore, there is a need to search for methods to reduce pesticide migration to the environment and incorporate new concepts. Thus it is purposeful to perform studies upon the application of sorption process on selected natural and waste materials as the

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[1] Department of Technology in Engineering and Environmental Protection, Białystok University of Technology, ul. Wiejska 45a, 15–351 Białystok, Poland, phone 85 746 9644, email: izoplana@wp.pl

shield for penetration of pesticides and metals (as pesticide constituents) into the environment, and to reduce their migration from other pesticide graveyard sites and stores [4, 5]. Phytoremediation on energetic plants was additional element that should limit the contaminants migration. The success of phytoremediation depends mainly on the properly selected plant species [6, 7]. Desirable features making possible to apply a given plant are: fast growth, producing large amounts of biomass in short time, developed root system, high tolerance to pollution, great ability to accumulate toxins in aboveground parts, resistance to diseases, pests, and weather conditions. All above requirements are met by energetic plants, the representative of which is Jerusalem artichoke (*Helianthus tuberosus* L.). This species does not require special soil conditions, thus its cultivation may be performed on chemically contaminated areas where production of consumption plants is not necessary. Jerusalem artichoke is utilized for energetic purposes as the fuel, for chipboards and compost production.

Present study was aimed at evaluating the usefulness of Jerusalem artichoke to phytoremediation of sorption subsoil (consisting of the soil and stabilized dairy sludge) contaminated with pesticides. In future, it would allow for applying the sorption screen around pesticide graveyard area, which reduces pesticide migration into the environment, and grown energetic plants – through phytoremediation – would prolong the sorbent vitality and remove pesticides accumulated in aboveground parts by means of combustion.

Material and methods

Investigations upon phytoremediation of sorption material were conducted under pot experiment conditions. The experimental design included 4 objects: control pot and 3 other pots containing soil amended with pesticides. The initial studies confirmed [4] the usefulness of soil mixture collected from pesticide graveyard area and stabilized dairy sewage sludge [8] to make a sorption shield around that site. Jerusalem artichoke was grown in 4 pots of 0.3 m^2 area and 90 dm^3 capacity filled with above mixtures (Fig. 1).

Fig. 1. Jerusalem artichoke (*Helianthus tuberosus* L.)

Sorption substrate consisting of a soil and dairy sewage sludge which characteristic is presented in Table 1.

Table 1

The characteristic of sewage sludge

Substance	[g · kg^{-1} d.m.]						
	[%]	Ca	Mg	total N		total P	
Manurial element		21.9	13.1	39.2		31.4	
Organic matter	66.5						
Heavy metal	[mg · kg^{-1} d.m.]						
	Pb	Cu	Cd	Cr	Ni	Zn	Hg
Content in sludge	3.3	24.3	0.15	10.9	3.8	137	0.12
Permisssible standard	500	800	10	500	100	2500	5

The vegetation period has lasted since spring till late autumn 2007. After acclimatization of plants, mixtures of chemically pure chloro- and phosphoorganic pesticides (aldrine, chloropropham, HCH, DDE, DDT, DDD, metoxychlor) were continuously added (which imitated surface supply) onto 3 experimental plots. During the whole experimental period, 5 mg of each active substance per pot was administered. After harvest, samples of soil, above- and underground parts of plants were collected. Pesticide concentrations were determined in collected samples in accordance to obligatory methodology using gas chromatograph coupled with mass spectrometer (GC/MS/MS 4000) as well as gas chromatograph AGILENT6890 equipped with ECD1 and NPD2 columns. Moreover, after sample digestion according to EPA 3015 procedure using microwave digester Mars 5, also metals concentrations (Cd, Cr, Cu, Ni, Pb and Zn) were determined by means of ICP-AES technique, and mercury content was determined by means of CV-AAS technique.

Results and discussion

Achieved results confirm observations made by Borkowska [9] and Styk [10], who found that Jerusalem artichoke, as perennial multipurpose species, is characterized by great yielding potential despite of poor soil and climatic requirements. Plants set in the first experimental year (set as several-year-old seedlings from a plantation) revealed high yields of aboveground parts. Opportunity to get high yields allows for proposing Jerusalem artichoke as one of the species useful for chemically degraded areas reclamation, particularly phytoremediation of pesticides from the sorption barrier.

Studies of Lunney et al [11] were to compare the ability of five plant varieties to mobilize and phytoremediation DDT and its metabolites. The potential and limitations of phytoremediation for removal of pesticides in the environment have been reviewed by Chaudhry et al [12].

Table 2

Mean concentration of pesticides and heavy metals in soil and Jerusalem artichoke

Pollutants	Limit detection	Control test			Test 1–3		
		Soil	Jerusalem artichoke		Soil	Jerusalem artichoke	
			stem	leaves		stem	leaves
Pesticides [mg · kg^{-1} d.m.]							
Aldrine	0.001	0.0097	—	—	0.1623	—	—
Chloroprophane	0.005	0.0178	—	—	0.1031	—	—
HCH	0.001	0.0669	0.0004	0.0008	0.1289	0.0021	0.0019
DDE	0.001	0.1599	0.0018	0.0011	0.3891	0.0101	0.0026
DDT	0.005	0.1909	0.0024	0.0011	0.3488	0.0073	0.0019
DDD	0.002	0.2270	0.0038	0.0007	0.3763	0.0180	0.0013
Metoxychlor	0.001	0.1120	0.0032	—	0.2647	0.0150	—
Metals [mg · kg^{-1} d.m.]							
Cd	0.06	0.079	—	0.143	< 0.06	0.070	0.111
Cr	0.3	7.721	—	0.667	7.714	0.481	0.623
Cu	8.0	55.638	—	11.898	10.147	5.311	8.321
Ni	1.2	5.021	—	0.957	3.212	0.609	1.725
Pb	1.0	71.426	—	0.439	7.347	0.591	0.845
Zn	6.0	65.055	—	23.337	21.123	20.161	28.032
Hg	0.001	0.056	—	0.016	0.048	0.018	0.021

Studies of Antoniewicz and Jasiewicz [13, 14] revealed high yielding potential of Jerusalem artichoke on the soil with varied heavy metals contamination, which proves its great resistance and fast adaptation to polluted soils. Own studies also confirmed results obtained by Borkowska [9], who observed more abundant yields of Jerusalem artichoke on substrate amended with sewage sludge than on mineral soil. It referred both to plant height and yield of biomass (Fig. 1). Besides high yield-forming potential, Jerusalem artichoke also shows a great ability to intake pesticides and heavy metals from the substrate. Much higher levels of absorbed pesticides were recorded in soil mixed with stabilized dairy sludge (0.10313–0.38909 mg · kg^{-1} d.m.) than in natural soil (0.01781–0.22702 mg · kg^{-1} d.m.). Similar dependence was observed in samples of Jerusalem artichoke above ground parts. Both leaves and stems of plant cultivated on sorption substrate accumulated more pesticides. Higher toxins concentrations were detected in stems (DDD 0.0180 mg · kg^{-1} d.m.) than in leaves (DDD 0.0013 mg · kg^{-1} d.m.), regardless the substrate Jerusalem artichoke was cultivated. Furthermore, metoxychlor was found in stems; it was not taken and accumulated by leaves both in “sorption” and control pots. It was symptomatic that Jerusalem artichoke takes only chloroorganic insecticides group from pots amended with pesticides, while aldrine, chloropropane, and pyrimicarb remained in the substrate.

Conclusions

Achieved results allow conclude that Jerusalem artichoke (*Helianthus tuberosus* L.) can be used for phytoremediation of soils contaminated with pesticides, and particularly to prolong vitality of sorption barrier around a pesticide graveyard area. More abundant yields of Jerusalem artichoke on the substrate amended with dairy sludge than mineral soil allows for predicting large amounts of a biomass for energetic purposes, thus removing accumulated pesticides by means of combustion.

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OCENA PRZYDATNOŚCI TOPINAMBURU (*Helianthus tuberosus* L.) DO FITOREMEDIACJI GLEBY ZANIECZYSZCZONEJ PESTYCYDAMI

Katedra Technologii w Inżynierii i Ochronie Środowiska
Politechnika Białostocka

Abstrakt: Celem pracy była ocena przydatności topinamburu (*Helianthus tuberosus* L.) do fitoremediacji podłoża sorpcyjnego zanieczyszczonego pestycydami. Obiektem badań było podłoże sorpcyjne, będące mieszaniną gleby oraz ustabilizowanego osadu mleczarskiego, przeznaczone do wykonania ekranu sorpcyjnego wokół mogilnika. Doświadczenie obejmujące 4 obiekty: kontrolę oraz 3 pozostałe zanieczyszczone pestycydami, prowadzono w wazonach o powierzchni 0,3 m^2 wypełnionych ww. mieszaniną, do których nasadzono topinambur. W badaniach wstępnych potwierdzono jego przydatność. Sezon wegetacyjny trwał od wiosny do późnej jesieni 2007 roku. Po okresie aklimatyzacji roślin do wazonów wprowadzano w stałych odstępach czasowych mieszaninę pestycydów chloro- i fosforoorganicznych. Po zbiorze roślin pobrano próbki podłoża oraz części naziemnych i podziemnych rośliny. W próbkach określano stężenie pestycydów zgodnie z obowiązującą metodyką. Stwierdzono, że zawartości pestycydów w podłożu sorpcyjnym (od 0,10313 do 0,38909 $mg \cdot kg^{-1}$ s.m.) były dużo większe niż w glebie kontrolnej (od 0,01781 do 0,22702 $mg \cdot kg^{-1}$ s.m.). Uzyskane wyniki pozwalają wstępnie stwierdzić, że topinambur może być wykorzystany do rekultywacji gleb zanieczyszczonych pestycydami, zwłaszcza do przedłużenia żywotności bariery sorpcyjnej wokół mogilnika. W przyszłości pozwoli to na zastosowanie wokół mogilnika ekranu sorpcyjnego, który zredukuje migrację pestycydów do środowiska, a uprawa fitoremediacyjnych roślin energetycznych umożliwi przedłużenie żywotności sorbentu i usuwanie pestycydów z części nadziemnych przez spalanie.

Słowa kluczowe: fitoremediacja, topinambur (*Helianthus tuberosus* L.), sorpcja, pestycydy, mogilnik

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Hanna JAWORSKA[1], Halina DĄBKOWSKA-NASKRĘT[1]
and Szymon RÓŻAŃSKI[1]

TOTAL CONTENT OF MERCURY IN ARABLE SOILS IN THE VICINITY OF LAFARGE-CEMENT POLAND SA PLANT ("KUJAWY" BIELAWY)

CAŁKOWITA ZAWARTOŚĆ RTĘCI W GLEBACH UPRAWNYCH W OTOCZENIU ZAKŁADÓW LAFARGE-CEMENT POLSKA SA, ZAKŁAD „KUJAWY" W BIELAWACH

Abstract: In the area of Kujawy-Pomerania province in Bielawy town the limestone is exploited which is the main resource in the production process carried out by Lafarge-Cement Plant. The alkaline reaction of emitted dusts caused excessive alkalisation of the surrounding soils which are also simultaneously contaminated by trace metals (including mercury).

The aim of the study was to assess the impact of Lafarge-Cement Poland SA Plant ("Kujawy" Bielawy) activity on total content of mercury in arable soils in the vicinity of the plant.

As a research material served arable soil gathered at various distances from the plant. Samples were collected from surface (0–20 cm) and subsurface (20–40 cm) horizons. Moreover samples were also collected from two soil profiles classified as Haplic Luvisol (Piechcin) and Haplic Podzol (Krotoszyn). The total content of mercury was determined in solid samples by atomic spectrometry method using AMA 254 mercury analyser. The results were as follows: in the 0–20 cm horizons within the range of 11.20–27.09 $\mu g \cdot kg^{-1}$ and in 20–40 cm horizons – from 11.53 to 26.48 $\mu g \cdot kg^{-1}$. In profile samples, the total mercury content was within the range of 3.89–27.15 $\mu g \cdot kg^{-1}$. In the Haplic Luvisol the highest total content of Hg was detected at the C horizon, the lowest however at Eet horizon. In the case of the Haplic Podzol, the highest concentration of Hg was found in surface and subsurface horizons. The assessment of the total mercury content in soils surrounding Lafarge-Cement Poland SA Plant, did not confirm the influence of cement dusts on mercury contamination.

Keywords: soils, alkalisation, mercury, dusts

From among various substances which have negative impact on the environment, mercury compounds are worthy of interest. This metal is transported from the sources mainly into the atmosphere, and from there it can cover large distances in the form of

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[1] Department of Soil Science and Soil Protection, University of Technology and Life Sciences, 85–029 Bydgoszcz, ul. Bernardyńska 6, Poland, phone 52 374 9512, email: hjawor@.utp.edu.pl

gas, dust or aerosols [1, 2]. In Poland the main sources of mercury are: combustion of fossil fuels, disposal of fluorescent lamps and batteries, production and application of mercury fungicides as well as the cement production [2–4].

Natural level of mercury content in environment is several times lower than the amounts initiated in anthropogenic way [2, 5, 6], that is why it is necessary to monitor the content of this metal in arable soils surrounding such plants as Lafarge.

In the area of Kujawy-Pomerania province in Bielawy town the limestone is exploited which is the main resource in the production process carried out by Lafarge-Cement Plant. The alkaline reaction of emitted dusts caused excessive alkalisation of the surrounding soils which are also simultaneously contaminated by trace metals, including mercury.

The aim of the study was to assess the impact of Lafarge-Cement Poland SA Plant (“Kujawy” Bielawy) activity on total content of mercury in arable soils in the vicinity of the plant.

Material and methods

As a research material has served arable soil samples gathered at various distances from the Lafarge plant. The samples were taken from surface (0–20 cm) and subsurface (20–40 cm) horizons and additionally collected from two soil profiles classified as Haplic Luvisol (Piechcin) and Haplic Podzol (Krotoszyn) according to World Reference Base for Soil Resources.

In the dried and sieved material (diameter below 2 mm) the following soil properties were determined: pH in H_2O and in 1 mol · dm^{-3} KCl solution, the total content of organic carbon and the content of $CaCO_3$ using commonly applied methods in soil science. Soil texture was determined according to the Casagrande areometric method, modified by Proszynski. Interpretation of the texture results was performed according to USDA classification. The total content of mercury was determined in solid samples with atomic spectrometry method using AMA 254 mercury analyser [7]. The analysis was triplicated and the results are an arithmetic mean (SD below 5 %).

The accumulation factor was also calculated as the ratio of Hg content in genetic horizon to its content in parent material.

Results and discussion

The texture of the analysed soils (Table 1) allows to categorise them as light soils in the surface (0–20 cm) and subsurface horizons (20–40 cm) in which the texture of loamy sand was found (USDA). The exception was found for the samples taken from Wolice I and Wolice II, where in both places sandy loam occurred (Table 1). Profile samples were characterised by loamy sand, except for the Piechcin profile (Table 2) where the C horizon was classified as sandy loam (USDA).

Depending on the sampling site, pH varied within the range of pH_{H_2O} 5.88–8.17 and pH_{KCl} 5.17–7.68 (Table 1). Alkaline pH was found in surface and subsurface samples in Sadlogoszcz (pH_{KCl} 7.58 and 7.68) and in Piechcin (pH_{KCl} 7.15 and 7.02) located closest to the plant. Moreover, alkaline pH also occurred in surface samples (pH_{KCl} 7.57) and subsurface samples (pH_{KCl} 7.60) taken from the site in Dabrowka Chelminska located beyond the plant impact area, and which could be the result of lime application. However, in the profile samples the pH is quite levelled (Table 1). In the Haplic Luvisol the lowest value was found in the Bt horizon (pH_{H_2O} 5.99 and 5.89), whereas in the Haplic Podzol – at the horizon of parent material (pH_{H_2O} 6.29 and 6.29).

Table 1

Physicochemical properties of soils

Sampling site	Depth [cm]	Share of fraction [%] with diameter [mm]			Organic C	$CaCO_3$	pH	
		2–0.05	0.05–0.002	< 0.002	$[g \cdot kg^{-1}]$		H_2O	KCl
Piechcin	0–20	79	6	15	4.1	n.d.*	7.32	7.15
	20–40	77	7	16	4.8	n.d.	7.32	7.02
Sadłogoszcz	0–20	85	10	5	5.2	102	7.98	7.58
	20–40	83	10	7	5.4	93	8.17	7.68
Krotoszyn	0–20	77	14	9	4.7	n.d.	6.28	5.74
	20–40	79	10	11	1.7	n.d.	6,44	5.88
Wolice I	0–20	63	20	17	4.5	n.d.	6.46	5.83
	20–40	60	21	19	5.2	n.d.	6.49	5.59
Wolice II	0–20	64	20	16	7.8	n.d.	6.43	5.74
	20–40	64	21	15	5.2	n.d.	6.40	5.56
Mamlicz	0–20	83	19	8	5.1	n.d.	5.88	5.21
	20–40	74	8	8	3.5	n.d.	6.20	5.17
Dabrowka Barcinska	0–20	78	15	9	16.0	51	7.64	7.57
	20–40	78	13	9	7.7	16	7.87	7.60

* n.d. – not detected.

The content of organic carbon in surface horizons ranged from 4.1 to 16.0 $g \cdot kg^{-1}$, and in the humus horizons of the profile samples equalled to 4.5 $g \cdot kg^{-1}$ in Haplic Podzol and 6.6 $g \cdot kg^{-1}$ in Haplic Luvisol. These are typical values for the soils of this region [9]. In the majority of the studied samples no presence of $CaCO_3$ was detected, except for two sampling sites where $CaCO_3$ was found in surface and in subsurface horizons, 10.2 % and 5.1 % as well as 9.3 % and 1.6 %, respectively. In profile samples (Table 2) however, only in the Piechcin profile was the content of $CaCO_3$ detected in surface and subsurface horizons, and equalled to 5.9 % and 5.0 %, respectively. The parent material of the soils in the vicinity of the plant does not contain $CaCO_3$, hence its presence in surface horizons is of anthropogenic origin.

The total content of Hg in soils layers varied in similar ranges as follows: in the 0–20 cm horizons from 11.20 to 27.09 $\mu g \cdot kg^{-1}$ and in 20–40 cm horizons – from 11.53 to 26.48 $\mu g \cdot kg^{-1}$ (Table 3).

Table 2

Physicochemical properties of soils

Sampling site	Horizon	Depth [cm]	Share of fraction [%] with diameter [mm]			Organic C [g · kg^{-1}]	CaCO$_3$ [%]	pH	
			2–0.05	0.05–0.002	< 0.002			H$_2$O	KCl
Piechcin	Ap	0–38	84	10	6	4.1	n.d.*	6.26	6.44
	Eet	38–93	93	2	5	4.8	n.d.	5.21	5.39
	Bt	93–120	81	7	12	5.2	n.d.	5.99	5.89
	C	> 120	68	16	16	5.4	n.d.	6.21	6.29
Krotoszyn	Ap	0–35	89	6	5	4.7	5.9	6.22	6.40
	Ees	35–50	88	6	6	1.7	5.0	6.02	6.51
	Bhfe	50–120	96	3	1	4.5	n.d.	5.99	5.89
	C	120–135	84	5	11		n.d.	6.29	5.29

* n.d. – not detected.

Table 3

Total extractable Hg content in soils

Sampling site	Depth	
	0–20 cm	20–40 cm
	Hg content [μg · kg^{-1}]	
Piechcin	16.87	18.02
Sadlogoszcz	11.20	11.53
Krotoszyn	21.93	13.98
Wolice I	23.79	25.58
Wolice II	27.09	26.48
Mamlicz	15.80	14.36
Dabrowka Barcinska	21.58	23.43

These values were quite levelled and did not confirm higher content of this metal in surface samples, as observed by other researchers [9, 10]. Higher total Hg content was found in samples rich in clay fraction (∅ < 0.002 mm), which should be related to this metal being bound by clay minerals [9, 10].

In profile samples (Table 4), the total mercury content was within the range of 3.89–27.15 μg · kg^{-1}. In Haplic Luvisol the highest total content of Hg was detected at the C horizon, the lowest however at Eet horizon, which could result from its lessivage and binding by mineral colloids [11]. Accumulation of Hg in deeper horizons, with lower humus content and higher clay fraction content, may lead to absorption of Hg in exchangeable form [12]. In Haplic Podzol the highest concentration of Hg was found in surface horizons, which could result from binding this metal by organic matter [9, 10].

Table 4

Total Hg content in soil profiles (SD < 5 %)

Sampling site	Horizon	Depth [cm]	Hg [$\mu g \cdot kg^{-1}$]	Accumulation factor
Piechcin	Ap	0–38	11.51	0.52
	Eet	38–93	3.89	0.17
	Bt	93–120	12.01	0.54
	C	> 120	22.25	
Krotoszyn	Ap	0–35	26.07	1.66
	Ees	35–50	27.15	1.73
	Bhfe	50–120	4.14	0.26
	C	> 120	15.66	

In order to illustrate the sources of Hg pollution of the analysed soils, Hg accumulation factors in soil profile were calculated (Table 4) (the ratio of Hg content in genetic horizon to its content in parent material). In Haplic Luvisol these factors were highest in Bt (0.54) and Ap horizons (0.52), whereas in the Haplic Podzol, in Ees (1.73) and Ap horizons (1.66). The values of these factors in surface horizons of the Haplic Podzol, indicate significant participation of anthropogenic Hg in the total content of this element [13].

The average content of Hg in the analysed soils is below its natural content in the soils of Poland, which is within 50–300 $\mu g \cdot kg^{-1}$ [4] and is also lower than its permissible level in soils used for ecological cultivation (1000 $\mu g \cdot kg^{-1}$) and the borderline level for agricultural areas (2 $mg \cdot kg^{-1}$) [13, 14]. That is why the analysed soils were qualified as non contaminated by this metal.

Conclusions

The texture of the analysed soils allows to classify them as light soils, with the content of organic carbon typical for these soils. The pH varied, depending on location of the sampling sites. Alkaline pH was found in surface and subsurface horizons of samples located closest to the plant. The detected $CaCO_3$ in several samples is of anthropogenic origin.

Total content of Hg in soils was as follows: in 0–20 cm horizons it ranged between 11.20 and 27.09 $\mu g \cdot kg^{-1}$ and in 20–40 cm horizons – 11.53 and 26.48 $\mu g \cdot kg^{-1}$. In profile samples, the values ranged between 3.89 and 27.15 $\mu g \cdot kg^{-1}$. The content allows to qualify the soils as non-contaminated.

The assessment of total mercury content in soils in the vicinity of the plant in Bielawy did not reveal the influence of cement dusts on Hg contamination in soils of the area.

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CAŁKOWITA ZAWARTOŚĆ RTĘCI W GLEBACH UPRAWNYCH W OTOCZENIU ZAKŁADÓW LAFARGE-CEMENT POLSKA SA, ZAKŁAD „KUJAWY” W BIELAWACH

Katedra Gleboznawstwa i Ochrony Gleb
Uniwersytet Technologiczno-Przyrodniczy w Bydgoszczy

Abstrakt: Celem podjętych badań była ocena wpływu Zakładów Cementowo-Wapienniczych „Lafarge” Zakład w Bielawach na całkowitą zawartość rtęci w glebach uprawnych w okolicy Zakładów.

Materiał badawczy stanowiły próbki gleb uprawnych, zlokalizowane w różnej odległości od Zakładów, które pobrano z dwóch głębokości oraz próbki pochodzące z dwóch profili glebowych, które zaklasyfikowano (wg PTG) jako: glebę płową typową (Piechcin) i bielicową właściwą (Krotoszyn). Całkowitą zawartość rtęci oznaczono metodą spektrometrii atomowej z wykorzystaniem analizatora AMA-254.

Badane gleby zaliczono do piasków gliniastych (PN-R-04033). Odczyn gleb był zróżnicowany w zależności od lokalizacji punktu badawczego – pH_{KCl} wahało się od 5,21 do 7,68. Zawartość C-organicznego mieściła się w zakresie 4,1–16,0 g · kg^{-1}. W większości badanych próbek nie stwierdzono obecności $CaCO_3$ z wyjątkiem dwóch punktów badawczych, w których $CaCO_3$ występował w poziomach wierzchnich, odpowiednio 10,2 % i 5,1 % oraz 9,3 % i 1,6 %. Natomiast jedynie w próbkach profilowych z Krotoszyna stwierdzono obecność $CaCO_3$ w wierzchnich poziomach: 5,9 i 5,0 %.

Całkowita zawartość Hg w glebach kształtowała się następująco: w poziomach 0–20 cm mieściła się w zakresie 11,20–27,09 µg · kg^{-1}, a w poziomach 20–40 cm – 11,53–26,48 µg · kg^{-1}. W próbkach profilowych, zawartości te wahały się w zakresie 3,89–271,50 µg · kg^{-1}. W większości badanych próbek większe całkowite zawartości Hg występowały w poziomach powierzchniowych, co może wynikać z zaabsorbowania tego metalu przez substancję organiczną i minerały ilaste. Średnia zawartość Hg w badanych glebach mieściła się poniżej zawartości naturalnej tego pierwiastka w glebach Polski, która wynosi 0,05–0,30 mg · kg^{-1}. Ocena całkowitej zawartości Hg w glebach z okolicy Zakładów w Bielawach nie wykazała wpływu pyłów cementowych na zanieczyszczenie rtęcią okolicznych gleb.

Słowa kluczowe: gleba, alkalizacja, rtęć, pyły

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Adam KACZOR[1], Grzegorz PAUL[1]
and Marzena S. BRODOWSKA[2]

EFFECT OF SEWAGE SLUDGE AND FLOTATION LIME ON FORMATION OF AVAILABLE FORMS OF PHOSPHORUS, POTASSIUM AND MAGNESIUM IN SOIL

ODDZIAŁYWANIE OSADU ŚCIEKOWEGO I WAPNA POFLOTACYJNEGO NA KSZTAŁTOWANIE SIĘ PRZYSWAJALNYCH FORM FOSFORU, POTASU I MAGNEZU W GLEBIE

Abstract: The influence of sewage sludge and flotation lime applied on three levels on the changes in the content of available forms of P, K and Mg was evaluated in the light soil from the vicinity of a former sulphur mine. The two-year pot experiment, which was set up using complete randomization method, was conducted on soil material with the granulometric composition of light loamy sand. Oat and spring rape were the test plants in the experiment. Prior to the experiment the soil was characterized by a strong acid reaction, low content of available phosphorus and potassium and very low content of available magnesium.

Obtained results show that experimental factors clearly differentiated the content of available forms of phosphorus, potassium and magnesium in soil. The content of phosphorus and magnesium in the test soil increased as the result of sewage sludge application and an opposite effect was observed in case of available potassium. By optimization of soil reaction, liming indirectly affected soil fertility in the available forms of analyzed nutrients.

Keywords: sewage sludge, flotation lime, available phosphorus, available potassium, available magnesium

Sewage sludge constitutes a valuable source of nutrients [1–3] and organic matter [4, 5]. However, it involves many hazards in the form of increased content of heavy metals and organic pollutants [4]. The environmental application of municipal sewage sludge may lead to sanitary danger and may cause chemical and biological contamination of soils, surface waters and even plants grown in the areas fertilized with the sludge [6]. In

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[1] Department of Biochemistry and Enviromental Chemistry, Faculty of Agriculture Sciences in Zamość, University of Life Sciences in Lublin, ul. Szczebrzeska 102, 22–400 Zamość, Poland, email: adam.kaczor@up.lublin.pl

[2] Department of Agricultural and Enviromental Chemistry, Faculty of Agricultural Bioengineering, University of Life Sciences in Lublin, ul. Akademicka 15, 20-950 Lublin, Poland, email: marzena.brodawska@up.lublin.pl

spite of above contradictions, agricultural and natural application of sewage sludge seems to be a rational method of usage and utilization [7]. Under the conditions of the deficiency of natural fertilizers, sewage sludge should be applied, in particular, for fertilization and improvement of the properties of low-quality soils [8] and for the reclamation of degraded lands. In the reclamation of chemically degraded and strongly acidified soils, alkaline wastes from the mining industry (eg lime resulted from sulphur flotation) are also applied.

The aim of the performed experiment was to analyze the effect of sewage sludge and flotation lime on the changes in the content of available forms of phosphorus, potassium and magnesium in light soil, obtained from the vicinity of a sulphur mine.

Material and methods

The experiment was set up on the soil material obtained from the arable layer of soil with a granulometric composition of light loamy sand. Two-year pot experiment was carried out using complete randomization method in the years 2004–2005. Prior to the experiment the soil obtained from the vicinity of a former sulphur mine was characterized by a strong acid reaction, low content of available phosphorus and potassium and a very low content of available magnesium. Two variable factors were used in the experiment: a dose of sewage sludge and a dose of flotation lime. Both factors were applied on three levels, according to the following pattern:

1. Ss_0Ca_0 4. Ss_1Ca_0 7. Ss_2Ca_0
2. Ss_0Ca_1 5. Ss_1Ca_1 8. Ss_2Ca_1
3. Ss_0Ca_2 6. Ss_1Ca_2 9. Ss_2Ca_2,

where:

Ss_0 – without sewage sludge application;
Ss_1 – sewage sludge applied in the amount of 10 $g \cdot kg^{-1}$ soil;
Ss_2 – sewage sludge applied in the amount of 20 $g \cdot kg^{-1}$ soil;
Ca_0 – no liming;
Ca_1 – flotation lime in the amount of 3.096 $g \cdot kg^{-1}$ soil;
Ca_2 – flotation lime in the amount of 6.192 $g \cdot kg^{-1}$ soil.

The sewage sludge used in the experiment had been obtained from the communal sewage treatment plant in Hajdow near Lublin and subjected to hygienization and stabilization with CaO prior to its application. It was established that the sewage sludge contained 17.42 $g\ P \cdot kg^{-1}$ of total phosphorus and total content of calcium and magnesium amounted 112.21 $g\ Ca + Mg \cdot kg^{-1}$.

Two test plants were cultivated on the analyzed soil: barley, ‘Cwal’ variety, in the year 2004 and spring rape, ‘Mozart “00”’ variety, in the year 2005. All experiment objects were also constantly fertilized with NPK and a microelement solution, in the amounts adjusted to the plants’ nutritional needs.

After the completion of the experiment on the soil content of available phosphorus and potassium was determined using Egnera-Riehm DL method, whereas the content of available magnesium was determined using the Schachtschabel method.

Results and discussion

The soil from the control series (Ss_0Ca_0) collected after the rape harvest in the flowering phase was characterized by the highest content of available forms of P, K and Mg (Table 1). In comparison with the status prior to the experiment set up, the phosphorus content was 2 times higher, potassium level was 4 times higher and magnesium content was nearly 5 times higher. This can be explained by the fact that the soil used in the experiment was not suitable for test plant cultivation, especially for rape – a plant with high requirements towards soil reaction [9]. The seed yields of this plant amounted to 0.27 g · pot^{-1}, and of straw was 0.74 g · pot^{-1}. Consequently, almost total inhibition in rape grown was accompanied by low uptake of the analyzed nutrients [10].

Table 1

The effect of sewage sludge and flotation lime on the soil content of available forms of phosphorus, potassium and magnesium

Determination	Available P	Available K	Available Mg
Object	[mg · kg^{-1}]		
Before the experiment	34.04	41.51	8.35
Soil after rape harvest in the flowering phase			
Ss_0Ca_0	67.39	166.34	40.38
Ss_0Ca_1	47.42	27.56	16.79
Ss_0Ca_2	61.20	22.48	22.46
Ss_1Ca_0	59.01	56.22	32.22
Ss_1Ca_1	57.14	25.75	23.15
Ss_1Ca_2	64.89	27.51	27.53
Ss_2Ca_0	58.86	44.42	42.99
Ss_2Ca_1	56.67	31.33	27.03
Ss_2Ca_2	72.35	25.14	30.63
Soil after rape harvest in the full maturity phase			
Ss_0Ca_0	65.12	91.82	27.58
Ss_0Ca_1	41.25	22.54	10.07
Ss_0Ca_2	43.43	18.94	13.41
Ss_1Ca_0	61.91	26.63	27.86
Ss_1Ca_1	47.08	16.75	13.44
Ss_1Ca_2	50.33	17.81	13.44
Ss_2Ca_0	61.59	19.48	28.02
Ss_2Ca_1	51.74	17.86	17.27
Ss_2Ca_2	61.59	16.43	18.35

The application of flotation lime – especially in series without sludge – was connected with an observable decrease in phosphorus, potassium and magnesium content in soil after the end of the experiment. The liming applied in the lower dose caused on average 1.26 times decrease in phosphorus content, 2.73 times decrease in potassium content and 1.97 times decrease in magnesium content, in comparison with their levels in the objects without liming. After the application of the higher lime dose, the corresponding values amounted to 1.19, 3.13 and 1.67, respectively. The decrease in the analyzed elements in soil results, to a large degree, from the yield-forming influence of lime, which was accompanied by the increase in plant uptake of the analyzed elements [10]. The decrease in available magnesium content in the soil might have also been influenced by liming, as it was in research carried out by Labuda et al [11] and Labetowicz and Szulc [12]. It can be caused by antagonism occurrence between Mg^{2+} and Ca^{2+} ions, which in consequence leads to the decrease in magnesium availability for plants [13].

The influence of sewage sludge on the level of analyzed elements in the soil – in comparison with flotation lime – was more differentiated and multidirectional. The direction and range of changes in these elements content were determined by the kind of examined cation, the timing of soil sample collection, sludge dose and lime application. The multidirectional character of this influence on the one hand was also connected with the fact that sewage sludge is the source of all the analyzed elements, especially of phosphorus [14], and on the other one this waste distinctly affected the increase of plant yields [10].

The sludge application in series without liming was connected with the decrease in available phosphorus content in soil. On the other hand, in limed series – as reported by other authors [7, 15] – the sludge caused the increase in this element in soil. This increase, according to the dose of sludge, reached on average 1.14–1.26 times, in comparison with the contents in the objects without sludge.

In most of the objects, the sewage sludge application affected the decrease in available forms of potassium content in the test soil. Similar connections were also observed by Grzywnowicz and Strutynski [16] and by Krzywy et al [17] in their researches. The decrease amounted on average 1.65 and 2.72 times, in series Ss_1 and Ss_2, respectively, in comparison with the values from control objects. It must be added that the greater decrease in the content of available potassium in soil was observed in objects with sludge, where liming was not applied at the same time. In the soil from under the plants harvested in the flowering phase, in objects Ss_1Ca_2, Ss_2Ca_1 and Ss_2Ca_2 the minor increase of available phosphorus was noticed, in comparison with the contents in control objects Ss_0Ca_0.

The content of available magnesium in soil as the result of sewage sludge application visibly increased. This increase – in comparison with the values from control objects without sludge – equaled on average 1.19 times with application of the lower dose of sewage sludge and 1.36 times with the higher one. The greater increase of magnesium in soil was noticed in limed series with double dose of sewage sludge. The obtained data are comparable to the results of Baran et al [15] and Krzywy and co-authors [17].

Conclusions

1. Sewage sludge and floatation lime application have distinctly differentiated the content of available forms of phosphorus, potassium and magnesium content in soil.

2. The content of available forms of the analyzed elements in the limed soil was lower than in the soil of control objects. This testifies to the increasing availability of the analyzed elements and their use by the test plants, under conditions of varying soil reaction.

3. In most of the objects, the application of sewage sludge has resulted in an increase in the soil content of available forms of phosphorus and magnesium and a decrease in the content of the available forms of potassium.

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ODDZIAŁYWANIE OSADU ŚCIEKOWEGO I WAPNA POFLOTACYJNEGO NA KSZTAŁTOWANIE SIĘ PRZYSWAJALNYCH FORM FOSFORU, POTASU I MAGNEZU W GLEBIE

Katedra Biochemii i Chemii Środowiskowej
Wydział Nauk Rolniczych Uniwersytetu Przyrodniczego w Lublinie

Abstrakt: Oceniono wpływ osadu ściekowego oraz wapna poflotacyjnego, zastosowanych na trzech poziomach, na zmiany zawartości przyswajalnych form P, K i Mg w glebie lekkiej pochodzącej z okolic byłej kopalni siarki. Przeprowadzono dwuletni eksperyment wazonowy założony na materiale glebowym o składzie granulometrycznym piasku gliniastego, metodą kompletnej randomizacji. W doświadczeniu roślinami testowymi były owies i rzepak jary. Gleba przed doświadczeniem charakteryzowała się bardzo kwaśnym odczynem, małą zawartością przyswajalnego fosforu i potasu oraz bardzo małą zawartością przyswajalnego magnezu.

Uzyskane wyniki wskazują, że czynniki doświadczalne widocznie zróżnicowały zawartość przyswajalnych form fosforu, potasu i magnezu w glebie. W efekcie stosowania osadu, zwiększyła się zawartość fosforu i magnezu w glebie testowej, a przeciwny skutek obserwowano w przypadku potasu. Wapnowanie, poprzez optymalizację odczynu gleby, wpływało pośrednio na jej zasobność w przyswajalne formy analizowanych składników pokarmowych.

Słowa kluczowe: osad ściekowy, wapno poflotacyjne, fosfor przyswajalny, potas przyswajalny, magnez przyswajalny

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Tomasz KLEIBER[1], Andrzej KOMOSA[1]
and Alicja NIEWIADOMSKA[2]

OPTIMIZATION OF LAWN FERTILIZATION WITH NITROGEN.
PART II. NUTRIENT STATUS OF PLANTS

OPTYMALIZACJA NAWOŻENIA TRAWNIKÓW AZOTEM.
CZ. II. STAN ODŻYWIENIA ROŚLIN

Abstract: The aim of the conducted investigations was to determine the effect of increasing nitrogen fertilization of lawns (at doses corresponding to 0, 50, 100, 150, 200 mg N $\cdot$ dm^{-3}) on the nutrient status of turf, nutrient uptake (nitrogen, phosphorus, potassium, calcium, magnesium and sulfur) and their quantitative proportions in aboveground parts of plants. A significant effect was found for fertilization with nitrogen on N, K and S nutrient status of plants, and a lack of such effect was recorded for P and Mg. A stimulating effect of nitrogen fertilization on nutrient uptake by aboveground parts of plants was observed. With an increase in the intensity of fertilization quantitative interrelations were recorded between nitrogen and the other macroelements (P, K, Ca, Mg and S). Nitrogen fertilization had a positive effect on the ornamental value of turf, which was most desirable when nutrient contents in aboveground parts of plants fell within the following ranges [%]: N 2.38–3.48, P 0.60–0.64, K 3.05–3.68, Ca 0.79–1.23, Mg 0.55–0.57 and S 0.45–0.55. These contents may be treated as temporary index nutrient contents for lawns.

Keywords: nitrogen fertilization, lawn, nutrient status, macroelements, nutrient uptake

Nitrogen, particularly its nitrate(V) form, belongs to nutrients which are relatively easily and rapidly leached from top soil layers deep into the soil profile. At the same time intensive fertilization with this nutrient is applied, among other things, in golf courses as well as football pitches. In turn, a lack of nitrogen fertilization is a major cause of the deteriorating appearance of lawns in green areas. It is commonly known that nitrogen fertilization has a significant effect on the appearance of plants, their yielding as well as uptake of the other nutrients [1–5].

The aim of the conducted investigations was to determine the effect of increasing nitrogen fertilization of lawns on the nutrient status of plants, nutrient uptake, as well as

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[1] Department of Horticultural Plant Nutrition, Poznan University of Life Sciences, ul. Zgorzelecka 4, 60–198 Poznań, Poland, email: tkleiber@up.poznan.pl, ankom@up.poznan.pl

[2] Department of Agricultural Microbiology, Poznan University of Life Sciences, ul. Szydłowska 50, 60–656 Poznań, Poland, email: alicja.niewiadomska@onet.eu

quantitative proportions of nutrients in aboveground parts of plants. Determination of temporary index nutrient contents in aboveground parts of plants, at which their ornamental value is most desirable, is an important parameter from the point of view of controlled nitrogen fertilization of the turf.

Material and methods

The vegetation experiment was conducted in the years 2007–2008 at the "Marcelin" Experimental Station of the Departments of the Faculty Horticulture, the Poznan University of Life Sciences. The analyses concerned the effect of increasing levels of nitrogen fertilization [mg N $\cdot$ dm^{-3}]: 0, 50, 100, 150, 200 (denoted as N-0 to N-200), corresponding to annual nitrogen doses of 0, 10, 20, 30 and 40 g N $\cdot$ m^{2}, on the macronutrient status of plants, as well as nutrient uptake and quantitative proportions of nutrients in aboveground parts of plants. Contents of the other macroelements in all analyzed combinations were supplemented to the standard levels [mg $\cdot$ dm^{-3}] of P 100, K 200, Mg 180 (2007) and 300 (2008) [6].

Experiment was conducted on a 2-year lawn, on which a lawn-seed mixture was sown at 25 g $\cdot$ m^{-2}, with the following composition: perennial ryegrass (*Lolium perenne* L.) 'Grasslands Nui' (45 %), tall fescue (*Festuca arundinacea* Schreb) 'Finelawn' (25 %), red fescue (*Festuca rubra* Hack.) 'Olivia' (10 %), red fescue (*Festuca rubra* Hack.) 'Boreal' (15 %), kentucky bluegrass (*Poa pratensis* L.) 'Balin' (5 %).

During the vegetation period samples of plant material, ie cut grass leaves, were collected for chemical analyses. Samples were collected individually, from each experimental plot (4 plots comprised 1 experimental combination) on the following dates: 26.07 and 03.09 (2007), 18.06, 23.07 and 25.08 (2008). Collected leaves were dried at 45–50 ^{o}C and next they were ground. In order to determine total N, P, K, Ca and Mg the plant material was mineralized in concentrated sulfuric acids, while for analyses of S content it was in a mixture of nitric(V) and chloric(VII) acids (3:1 v/v) [7]. After mineralization of plant material the following analyses were performed: N total – by distillation according to Kjeldahl in a Parnas–Wagner apparatus, P – by colorimetry with ammonium molybdate (according to Schillak), K, Ca, Mg – by AAS (in a Carl-Zeiss Jena apparatus), S – by nephelometry with $BaCl_2$. Results of chemical analyses of plants were analyzed statistically using the Duncan test (α = 0.05).

Results

A significant effect of nitrogen fertilization on the nutrient status of plants in terms of this nutrient was observed (Table 1). Total nitrogen content in aboveground parts of plants, in case of the N-0, N-50 and N-100 combinations, did not differ significantly (2.43, 2.25, 2.38 % N, respectively). In case of the N-50 combination a trend was found, although not proven statistically, for nitrogen content to decrease in leaves, probably caused by the so-called Steenbjerg effect. The most advantageous nutrient status of plants in case of nitrogen was recorded in case of the N-200 combination (3.48 % N).

Table 1

The effect of nitrogen fertilization on contents of nitrogen, phosphorus and potassiu min aboveground parts of plants [% d.m.]

N level (A)	N			P			K		
	Year								
	2007	2008	Mean	2007	2008	Mean	2007	2008	Mean
N-0	2.57a	2.29a	2.43a	0.65a	0.57a	0.61a	3.43a	2.68a	3.06a
N-50	2.39a	2.11a	2.25a	0.60a	0.57a	0.59a	3.27a	2.67a	2.97a
N-100	2.45a	2.31a	2.38a	0.66a	0.54a	0.60a	3.29a	2.81a	3.05a
N-150	2.77b	2.85b	2.81b	0.71a	0.56a	0.64a	3.64b	3.07b	3.36b
N-200	3.50c	3.45c	3.48c	0.67a	0.54a	0.61a	4.01c	3.34c	3.68c
Mean	2.73a	2.60a		0.66a	0.56a		3.53b	2.91a	

* Values designated with the same letters within columns do not significantly differ at p = 0.05.

In contrast to nitrogen, no significant effect was shown of increasing fertilization on the nutrient status of aboveground parts of plants in case of phosphorus. Contents of this nutrient ranged from 0.59 % (in the N-50 combination) to 0.64 % P (in the N-150 combination). Nutrient status of plants for phosphorus in successive years of the study was similar (0.67 and 0.54 % P, respectively).

Increasing nitrogen fertilization significantly differentiated nutrient status of plants for potassium. As in case of total nitrogen, a similar nutrient status for this nutrient was found in case of combinations N-0, N-50 and N-100 (3.06, 2.97 and 3.05 % K, respectively). The best nutrition with potassium was observed for plants in case of combination N-200 (3.68 % K). The year of the study significantly modified the content of this nutrient in aboveground parts of plants. It was significantly higher in the first year of the study (3.53 % K) in comparison with the second year (2.91 % K).

A significant variation in calcium status of plants was found, depending on the level of nitrogen fertilization. The lowest calcium content was determined for combination N-200 (0.79 % Ca), while the highest (1.23 % Ca) in combination N-100. Nutrient status for this element was similar in successive years of the study (1.07 and 0.94 % Ca, respectively).

Nitrogen fertilization did not modify the nutrient status of plants in case of magnesium. Contents of this element in aboveground parts of plants ranged from 0.52 % (for N-0) to 0.57 % Mg (for N-200). A significant improvement was found in the nutrient status of plants for magnesium in 2008 (0.59 % Mg) in comparison to that of 2007 (0.50 % Mg).

Nitrogen fertilization had a positive effect on sulfur status of plants (Table 2). The biggest amount of this nutrient was determined in case of combination N-200 (0.55 % S). The other combinations did not differ significantly, falling within the range from 0.44 % (for N-50) to 0.47 % S (for N-0). Probably the best nutrient status of plants for sulfur in case of combination N-200 was caused by the application of the highest doses of sulfur as ions accompanying in magnesium fertilization (magnesium sulfate) and potassium fertilization (potassium sulfate).

Table 2

The effect of nitrogen fertilization on contents of calcium, magnesium and sulphur in aboveground parts of plants [% d.m.]

N level (A)	Ca			Mg			S		
	Year								
	2007	2008	Mean	2007	2008	Mean	2007	2008	Mean
N-0	0.91b	0.99a	0.95ab	0.48a	0.55a	0.52a	0.40a	0.54a	0.47a
N-50	1.25c	0.93a	1.09b	0.51a	0.59bc	0.55a	0.37a	0.51a	0.44a
N-100	1.41c	1.05a	1.23b	0.51a	0.58b	0.55a	0.38a	0.53a	0.45a
N-150	1.05b	0.88a	0.97ab	0.49a	0.62cd	0.56a	0.35a	0.58a	0.46a
N-200	0.75a	0.83a	0.79a	0.50a	0.63d	0.57a	0.53a	0.57a	0.55b
Mean	1.07a	0.94a		0.50a	0.59b		0.40a	0.55b	

* Values designated with the same letters within columns do not significantly differ at $p = 0.05$.

Concluding remarks. A significant effect was found of increasing nitrogen fertilization in doses ranging from 0 to 40 g $N \cdot m^{-2}$ (corresponding to 0–200 mg $N \cdot dm^{-3}$) on nutrient status of the lawn in case of nitrogen, potassium and sulfur. Such an effect was not shown for phosphorus and magnesium. In case of sulfur no marked trend was observed for changes in its contents. The most desirable ornamental value of the lawn was found at the following nutrient contents in aboveground parts of plants [% d.m.]: N 2.38–3.48, P 0.60–0.64, K 3.05–3.68, Ca 0.79–1.23, Mg 0.55–0.57 and S 0.45–0.55.

Nutrient uptake. A significant effect of increasing nitrogen fertilization on nutrient uptake by aboveground parts of plants was observed (Table 3). The lowest net uptake was determined in case of the control combination (N-0), with no nitrogen fertilization. The biggest nutrient uptake was found for the combination with the most intensive nitrogen fertilization (N-200), which stimulated – in comparison with combination N-0 – an increase in uptake by [%]: N (+330.7), P (+202.6), K (+263.0), Ca (+150.0), Mg(+227.3) and S (+251.0).

Table 3

The effect of nitrogen fertilization on nutrient uptake by aboveground parts of plants [g m^2] (total for years 2007+2008)

Nutrient	N level					
	N-0	N-50	N-100	N-150	N-200	Mean
N	15.3a	20.4a	28.1b	42.9b	65.9c	34.5
P	3.8a	5.3a	7.1b	9.8bc	11.5c	7.5
K	19.2a	26.9a	36.0a	51.3b	69.7c	40.6
Ca	6.0a	9.9a	14.5b	14.8b	15.0b	12.0
Mg	3.3a	5.0a	6.5b	8.6b	10.8c	6.8
S	2.9a	4.0a	5.4b	7.1b	10.4c	6.0

* Values designated with the same letters within rows do not significantly differ at $p = 0.05$.

Relations between nutrients. A modifying effect of nitrogen fertilization on quantitative relationships between nutrients in aboveground parts of plants was observed in this study (Table 4). With an increase in nitrogen fertilization the following ratios were observed to decrease: the N : P ratio (from 1.00 : 0.25 to 1.00 : 0.18), N : K (from 1.00 : 1.26 to 1.00 : 1.06), N : Ca (from 1.00 : 0.39 to 1.00 : 0.23), N : Mg (from 1.00 : 0.21 to 1.00 : 0.16) and N : S (from 1.00 : 0.19 to 1.00 : 0.16).

Table 4

The effect of nitrogen fertilization on relations between components in aboveground parts of plants (means for 2007–2008)

Nutrient	N level				
	N-0	N-50	N-100	N-150	N-200
N	1.00	1.00	1.00	1.00	1.00
P	0.25	0.26	0.25	0.23	0.18
K	1.26	1.32	1.28	1.20	1.06
Ca	0.39	0.48	0.52	0.35	0.23
Mg	0.21	0.24	0.23	0.20	0.16
S	0.19	0.19	0.19	0.16	0.16

Discussion

In this study, depending on the level of nitrogen fertilization, nutrient contents in aboveground parts of plants were found to be [% d.m.]: N 2.25–3.48, P 0.59–0.64, K 2.97–3.68, Ca 0.79–1.23, Mg 0.52–0.57 and S 0.44–0.55. Similar contents of nitrogen, potassium, magnesium and markedly lower contents of phosphorus and calcium were recorded in case of perennial ryegrass in pure sowing [8].

A positive and stimulating effect of nitrogen fertilization was found on the uptake of this nutrient by aboveground parts of plants, which confirms earlier studies [1] for doses ranging from 0 to 500 kg N $\cdot$ ha^{-1}. Moreover, a significant effect on nitrogen uptake by ryegrass as well as its yielding was found for lower doses, up to 200 kg N $\cdot$ ha^{-1} [5]. A strong response of ryegrass to nitrogen fertilization was observed [2]. This is evident particularly in the initial stage of plant development, which affects the formation and development of inflorescences – and which is used in seed plantations of this species [9]. A positive effect of nitrogen fertilization on nutrient status of grasses for this nutrient was confirmed in earlier studies [10]. At the same time the authors determined a reduction in the contents of the other macroelements in plants, ie phosphorus, potassium, calcium, magnesium and sulfur.

The effect of nitrogen fertilization on nutrient status was also investigated in case of other horticultural species. High levels of nitrogen fertilization had a negative effect on potassium uptake by *Geranium sylvaticum* [11]. Moreover, increased contents of nitrogen, calcium, magnesium, sulfur and sodium in biomass of Virginia fanpetals were recorded under the influence of increasing doses of nitrogen (ranging from 0 to 150 kg N $\cdot$ ha^{-1}), at a constant fertilization with phosphorus (80 kg P_2O_5) and potassium (120 kg K_2O) [3, 4]. In turn, high contents of nitrogen in the substrate (100–200 mg $N \cdot dm^{-3}$) in case of pelargonium (*Pelargonium xhortorum*) caused an increase in contents of soluble forms of nitrogen, calcium and magnesium in some parts of plants [12]. Earlier studies showed [13] that increasing nitrogen fertilization (at doses ranging from 0 to 200 kg $N \cdot ha^{-1}$) had a significant effect on an increase in nitrogen content in dry matter of tubers in sunflower (*Helianthus tuberosus*); moreover, it significantly modified contents of calcium and sodium.

Conclusions

1. A significant effect of nitrogen fertilization on nutrient status of aboveground parts of the lawn was found in case of nitrogen, potassium and sulfur. Nitrogen fertilization did not modify phosphorus and magnesium status of plants.
2. A positive and stimulating effect of nitrogen fertilization was shown for nutrient uptake by aboveground parts of plants. The lowest uptake was determined in case of the control combination (N-0), while the highest in the combination with the most intensive nitrogen fertilization (N-200).
3. Nitrogen fertilization modified quantitative proportions between nutrients in aboveground parts of plants. With an increase in fertilization with this nutrient the N:P, N:K, N:Ca, N:Mg and N:S ratios decreased.
4. The most desirable ornamental value was found for the turf, containing in aboveground parts of plants the following amounts of nutrients [% d.m. aboveground parts of plants]: N 2.38–3.48, P 0.60–0.64, K 3.05–3.68, Ca 0.79–1.23, Mg 0.55–0.57 and S 0.45–0.55.

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OPTYMALIZACJA NAWOŻENIA TRAWNIKÓW AZOTEM.
CZ. II. STAN ODŻYWIENIA ROŚLIN

Katedra Nawożenia Roślin Ogrodniczych, Katedra Mikrobiologii Rolnej,
Uniwersytet Przyrodniczy w Poznaniu

Abstrakt: Celem przeprowadzonych badań było określenie wpływu wzrastającego nawożenia azotem trawnika (w dawkach odpowiadających 0, 50, 100, 150, 200 mg N · dm^{-3}) na stan odżywienia murawy, pobranie składników pokarmowych (azotu, fosforu, potasu, wapnia, magnezu i siarki) oraz wzajemne relacje ilościowe między nimi w częściach nadziemnych roślin. Stwierdzono znaczny wpływ nawożenia azotem (w formie NH_4NO_3) na stan odżywienia roślin N, K i S, a brak takiego wpływu w przypadku P i Mg. Zaznaczył się stymulujący wpływ nawożenia azotem na pobranie składników pokarmowych przez części nadziemne roślin. Wraz ze wzrostem intensywności nawożenia osłabieniu ulegały wzajemne relacje ilościowe między azotem a pozostałymi makroelementami (P, K, Ca, Mg, S). Nawożenie azotowe wpływało pozytywnie na walory dekoracyjne murawy, które były najkorzystniejsze, gdy zawartości składników pokarmowych w częściach nadziemnych roślin kształtowały się w zakresie [%]: N 2,38–3,48; P 0,60–0,64; K 3,05–3,68; Ca 0,79–1,23; Mg 0,55–0,57 oraz S 0,45–0,55. Zawartości te można traktować jako tymczasowe zawartości wskaźnikowe składników pokarmowych dla trawników.

Słowa kluczowe: nawożenie azotem, trawnik, stan odżywienia, makroelementy, pobranie składników

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Michał KOPEĆ[1], Marta KACZMARCZYK[1]
and Jan ZARZYCKI[2]

CONTENT OF EXCHANGEBALE CATIONS IN GRASSLAND SOIL DEPENDING ON HABITAT CONDITIONS IN THE RADZIEJOWA RANGE

ZAWARTOŚĆ KATIONÓW WYMIENNYCH W GLEBIE UŻYTKÓW ZIELONYCH W ZALEŻNOŚCI OD WARUNKÓW SIEDLISKOWYCH W PASMIE RADZIEJOWEJ

Abstract: The research has aimed to determine the contents and variation of exchangeable cations in the soil of grasslands in the Radziejowa range (The Beskid Sadecki Mountains). The investigations were conducted in the areas with diversified habitat conditions under various type of management. The plant community description considered the altitude above sea level, land slope and aspect, and botanical composition. In the soil taken from the 0.10 cm layer pH was determined in 1 mol KCl $\cdot$ dm^{-3} and exchangeable cations (Ca, Mg, K and Na) by means of extraction with 1 mol CH_3COONH_4 $\cdot$ dm^{-3}.

In the experiment the contents of exchangeable calcium forms in soil was conditioned by the altitude above sea level and the slope angle. Similar dependencies were found for the soil reaction. The soil reaction was changing and affected the concentrations of exchangeable cation forms. In soil sorption capacity the dominant alkaline cation was calcium whose concentration in the analyzed soils oscillated from 616 to 7325.79 mg Ca $\cdot$ kg^{-1} soil.

Keywords: exchangeable cations, soil reaction, habitat conditions

Soils constitutes the main link in the natural element cycling, including macroelements [1]. Changes in chemical composition of soils directly affect the plants and indirectly also influence animals and humans. An important factor shaping soil fertility, is their ability to meet plant nutritional requirements is the amount and bioavailability of nutrients. Exchangeable alkaline cations [2], which are treated as potentially available to plants, play an important role among them [3]. Soil fertility diversification in mountain

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[1] Department of Agricultural Chemistry, Agricultural University in Krakow, al. A. Mickiewicza 21, 31–200 Kraków; email: mprzetaczek@ar.krakow.pl

[2] Department of Ecology, Climatology and Air Protection, Agricultural University in Krakow.

soils depends to a great degree on the altitude and land slope. These properties may be directly reflected in diverse crop yields [4].

The aim of the presented paper is to reveal the variation range for alkaline cation resources in mountain soils in the Radziejowa Range considering the land slope and altitude above sea level.

Material and methods

The research was conducted in the Radziejowa Range (The Beskid Sadecki Mountains) in 2006. 210 samples were collected from grasslands with diversified habitat conditions and various types of management. Each time the altitude above sea level, land slope and slope aspect, and botanical composition were determined, and the plant communities were described. Dominant were acid brown soils (podzolic and typical) [5]. In the soil from the 0–10 cm layer pH was assessed in 1 mol KCl $\cdot$ dm^{-3} and exchangeable cations (Ca, Mg, K and Na) by means of extraction with 1 mol $CH_3COONH_4 \cdot$ dm^{-3}. Vegetation was described with Braun-Blanquet method on 100 m^2 research plots and the share of individual plant species was determined on the basis of an average area cover.

The research material was diversified considering habitat conditions (the altitude above sea level 360–960 m; land slope 0–40 ^{o}; pH 3.59–6.63; the share of grasses in the sward 6–87 %; the share of legumes 0–40 %).

Correlation coefficients, r and determination coefficients, r^2 were computed in order to present relationships between selected habitat properties of the researched soils. The results were presented in a graphic form and as statistical parameters determined using Statistica package No. JGNP0-5B493631AR.

Results and discussion

The reaction of discussed soils was strongly diversified (Table 1). On the basis of mean value of pH assessed in 1 mol KCl $\cdot$ dm^{-3}, the investigated soils may be counted among very acidic and acidic. Mean pH_{KCl} value was 4.28. Usually soil acidification causes worsening of its chemical properties. In the investigated soils pH value depended on the altitude and land slope (Fig. 1). Statistical analysis revealed this dependence on the significance level of $p = 0.01$ but the value of correlation coefficients was small (land slope $r = -0.146$, a.s.l. $r = -0.147$). The lowest pH value were noted from the altitude over 800 m a.s.l. at the land slope over 15 ^{o}. On the other hand at the altitude of 470–800 m a.s.l. at the land slope to 15 ^{o} pH value was the highest.

Backward stepwise multiple regression which analyzed the effect of factors on individual soil cations revealed an influence of soil reaction on the sum of exchangeable cations. It was found that in the soil from the investigated area the content of a half of bivalent cations and a quarter of univalent cations depended on the soil reaction. The higher the soil reaction values, the higher cation content in soil. Such condition was not found for altitude above sea level or the land slope.

Table 1

Statistical parameters of selected factors considered in environmental research

Parameter	pH	Land slope [^{o}]	Exchangeable cation content [mg/kg d.m.]				Sum of base cations [mmol(+) · kg^{-1}]
			Na^+	Mg^{++}	K^+	Ca^{++}	
Arithmetic mean	4.28	17.2	14.79	159.7	79.2	2205	125.7
Standard deviation	0.54	8.22	5.00	104.5	35.9	1235	67.2
Minimum	3.59	0	4.79	33.7	4.6	617	36.4
Maximum	6.53	40	52.23	752.6	249.1	7326	387.7
Lower quartile	3.91	10	12.03	96.8	54.5	1334	82.4
Upper quartile	4.49	20	16.43	189.6	95.1	2634	149.2
CV*	12.6**	47.8	33.8	65.5	45.4	56.0	53.4

* CV – coefficient of variability; ** CV – coefficient of logarithmic values.

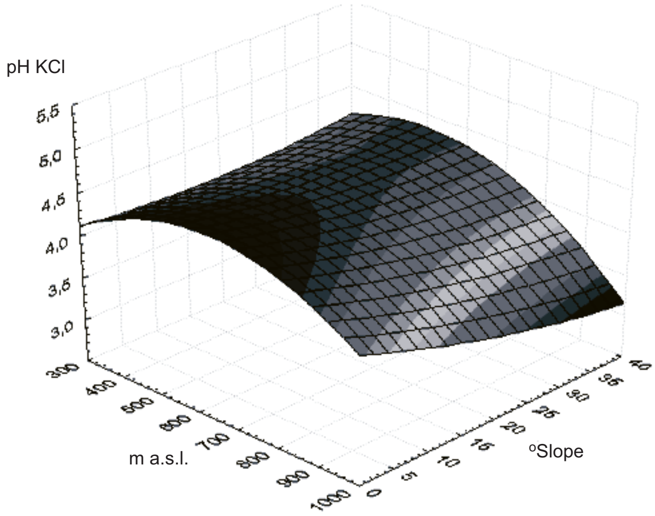

Fig. 1. Values of pH [1 mol KCl · dm^{-3}] in the investigated area depending on the altitude above sea level and land slope

With the slope angle increasing within the 0–25^{o} range, Na^+ concentrations in soil (Fig. 2) decreased with altitude. Above 25^{o} land slope, the content of this element did not change with increasing land altitude. Land slope had a greater effect on exchangeable sodium concentrations in soil than the altitude above sea level. At the land slope above 40^{o} the lowest content of this element was found. Exchangeable sodium concentrations in the analyzed soils was on the level of ca 15 mg Na · kg^{-1} of soil, however its variation was the smallest among the studied cations (Fig. 2, Table 1). Statistical analysis revealed a significant (on < 0.05 level) correlation of sodium exchangeable forms concentrations and land slope, soil reaction and carbon content in soil. This dependence was not found in relation to the altitude above sea level. Values of

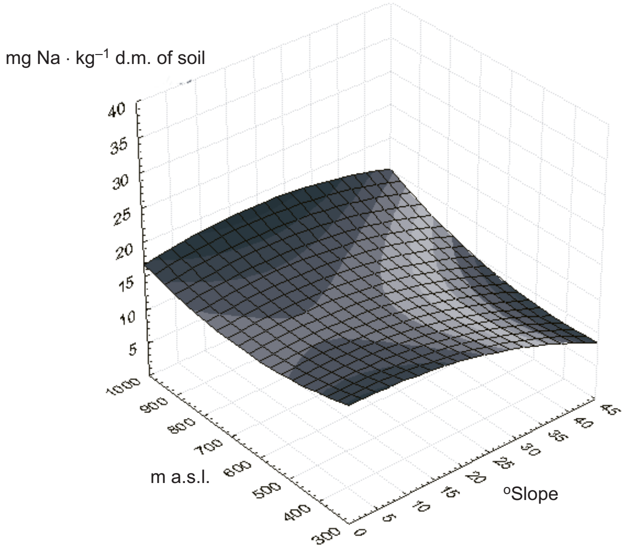

Fig. 2. Sodium concentrations in soil in 1 mol CH_3COONH_4 extract [mg · kg^{-1}] depending on the altitude above sea level and land slope

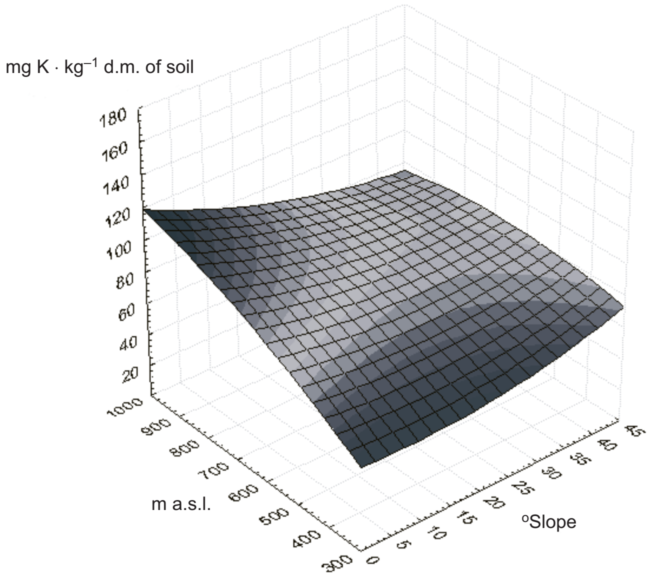

Fig. 3. Potassium concentrations in soil in 1 mol CH_3COONH_4 extract [mg · kg^{-1}] depending on the altitude above sea level and land slope

correlation coefficients of exchangeable sodium content in relation to land slope, pH and carbon content were respectively: –0.17; 0.41 and 0.53.

In the discussed soils land slope was not significantly important for the content of K^+ cations. Exchangeable potassium concentration in the analyzed soils was correlated with the soil reaction, altitude above sea level and carbon content (Fig. 3). Correlation coefficients for these factors were respectively: 0.25; 0.28 and 0.29. Increase in the content of exchangeable potassium content might be caused by this element displacement from more sparingly soluble minerals or compounds in result of stronger soil acidification, which occurred with altitude above sea level. Straczynska [6] pointed to this fact in her studies. The interval of this element exchangeable forms from 4.55 to 249 mg K · kg^{-1} d.m. was considerable but in case of quartiles range it diminished visibly (Table 1). Above 650 m a.s.l. (Fig. 3) a decrease in potassium content was detected along with increasing land slope. The highest concentrations were found on the terrains above the altitude of 800 m a.s.l. and at low land slope (up to 35 ^{o}). Under such conditions, greater moisture and accumulation of floatable particles along with diminishing land slope, soil sorption capacity increases favouring retaining greater contents of exchangeable potassium. According to Wrobel and Stanislawska-Glubiak [7] a higher concentration of K^+ ions in soil sorption complex may lead to dislodgement of bivalent ions from it, indirectly increasing soil acidification.

In the conducted research the contents of exchangeable forms of calcium and magnesium in soil was conditioned by the altitude above sea level and the slope angle (Fig. 4). Calcium was the dominant alkaline cation in sorption capacity, its content in

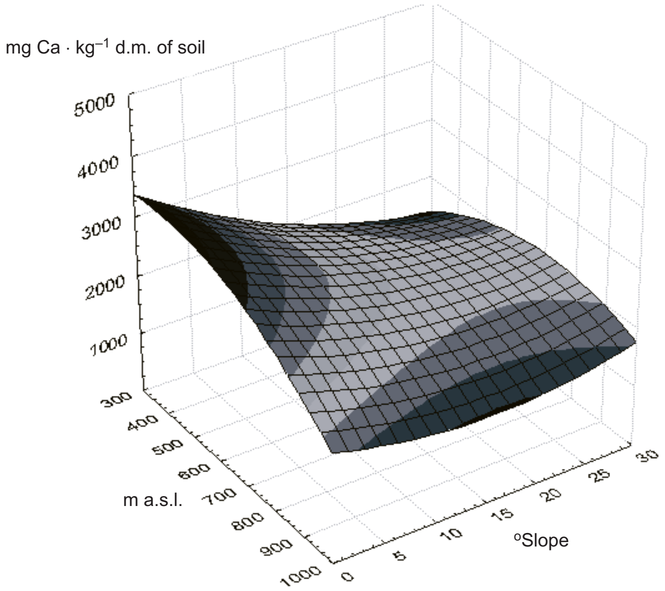

Fig. 4. Calcium concentrations in soil in 1 mol CH_3COONH_4 extract [mg · kg^{-1}] depending on the altitude above sea level and land slope

the analyzed soils ranged from 616 to 7325.79 mg Ca · kg of soil, which corresponds to between 15.41 and 183.14 mmol(+) · kg^{-1}. Kopec [8] confirms the lower values at the application of nitrogen fertilization and liming on the slope angle of 7^{o}, at the altitude of 720 m a.s.l. and NNE slope aspect in the experiment localized 30 km from the discussed experimental site.

According to Filipek and Dechnik [9] the degree of soil saturation with calcium cations depends on the slope aspect. In these authors' opinion soils on northern slopes reach the lowest Ca^{++} contents. Considering mean Ca^{++} content in the analyzed soils, they may be ordered as follows; soils from the: SW, NW, E, N,S, NE and SE slopes (Table 2). However, the differences between mean contents did were not statistically significant. No significant differences were found for Mg^{++}, either (Table 2).

Table 2

Mean concentrations of Mg^{++} and Ca^{++} depending on slope aspect

No.	Aspect	Mean contents of exchangeable cations [mg · kg soil]			
		Ca^{++}	LSD $\alpha < 0.05$	Mg^{++}	LSD $\alpha < 0.05$
1	N	1984	a	139.8	a
2	NE	2021	a	138.1	a
3	E	1899	a	164.7	a
4	SE	1841	a	160.1	a
5	S	2000	a	122.1	a
6	SW	1841	a	135.4	a
7	W	2128	a	166.7	a
8	NW	1890	a	138.2	a

Backward stepwise multiple regression tested the effect of independent factors, such as slope aspect, land slope, soil reaction, altitude a.s.l, insolation and C percent on the concentration of calcium cations in soil. Obtained equation with significant pH factor had the following parameters: r = 0.7094, r^2 = 0.5032, $F_{(3.186)}$ = 62.813, d < 0.0000 Stat. error estim. 883.22.

	BETA	Stat. error	B	Stat. error	t(187)	p level
Intercept			–4014.48	529.70	–7.578	0.000000
pH	0.550	0.057	1270.16	132.87	9.559	0.000000

Exchangeable calcium content in the analyzed soils was diminishing with the altitude (Fig. 4), however is was not confirmed by the statistical analysis. These parameters testify that calcium cation concentration in soil in the investigated area in a half depended on the soil pH. The higher the soil reaction values, the higher exchangeable Ca content in soil.

The variation range for magnesium in the discussed soils (Table 1) was smaller than in case of univalent cations. The multiple regression considering, the same features as for calcium (at parameters: $r = 0.7799$, $r^2 = 0.6083$, $F_{(3.186)} = 96.319$, $p < 0.0000$ Stat. error estim. 66.435) it was found that the content of this cation in 40 % depended on soil pH value and in 20 % on carbon concentrations. The higher the values of the analyzed factors, the higher exchangeable magnesium content in soils.

	BETA	Stat. error	B	Stat. error	t(187)	p level
Free intercept			–348.5	38.81	–8.98	0.000000
pH	0.419	0.051	81.9	10.09	8.11	0.000000
% C	0.195	0.051	17.8	4.68	3.80	0.000189

Exchangeable magnesium content in the soils from the investigated area was strongly correlated ($r = 0.630$) with the soil reaction and organic matter contents ($r = 0.50$).

Conclusions

The highest values of soil reaction were found at small land slope. Increase in pH value affects the content of exchangeable forms of alkaline cations.

The altitude above sea level and land slope have a lesser influence on the contents of exchangeable cations in soil than the soil reaction.

No effect of direction of slope angle on which the grassland was situated on the contents of exchangeable cations was evidenced.

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ZAWARTOŚĆ KATIONÓW WYMIENNYCH W GLEBIE UŻYTKÓW ZIELONYCH W ZALEŻNOŚCI OD WARUNKÓW SIEDLISKOWYCH W PASMIE RADZIEJOWEJ

[1] Katedra Chemii Rolnej i Środowiskowej
2 Katedra Ekologii, Klimatologii i Ochrony Powietrza
Uniwersytet Rolniczy im. H. Kołłątaja w Krakowie

Abstrakt: W prezentowanych badaniach określono zawartość i zmienność kationów wymiennych w glebie użytków zielonych w paśmie Radziejowej (Beskid Sądecki). Badania prowadzono na terenach o zróżnicowanych warunkach siedliskowych oraz o różnym sposobie gospodarowania. Przy opisie zbiorowiska określano wysokość nad poziom morza, nachylenie oraz ekspozycję i skład botaniczny. W glebie w warstwie 0–10 cm oznaczono pH w 1 mol KCl $\cdot$ dm^{-3} oraz kationy wymienne (Ca, Mg, K i Na), ekstrahując octanem amonu o stężeniu 1 mol $CH_3COONH_4 \cdot dm^{-3}$.

W przeprowadzonych badaniach zawartość wymiennych form wapnia w glebie była uwarunkowana wysokością nad poziom morza oraz nachyleniem stoku. Podobne zależności stwierdzono w przypadku odczyny gleby. Odczyn gleby ulegał zmianie i wpływał na zawartość wymiennych form kationów zasadowych. W pojemności sorpcyjnej dominującym kationem zasadowym był wapń, którego zawartość w analizowanych glebach waha się od 616 do 7325,79 mg Ca $\cdot$ kg^{-1} gleby.

Słowa kluczowe: kationy wymienne, odczyn gleby, warunki siedliskowe

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Bożena ŁOZOWICKA[1]

RISK AND THREAT FOR HEALTH CONSUMERS BY PESTICIDE RESIDUES IN CROPS FROM NORTH-EASTERN POLAND

ZAGROŻENIE ZDROWIA KONSUMENTÓW POZOSTAŁOŚCIAMI PESTYCYDÓW Z PŁODÓW ROLNYCH PÓŁNOCNO-WSCHODNIEJ POLSKI

Abstract: Maximum residue levels of pesticides (MRL), as obligatory normative values appeared in the Polish food-legislation in 1993. Among at present obligatory values (MRL) one differentiates values implemented from Instructions of the European Union and so called national MRL (the Order of The Minister of Health from the day 16 May 2007). One of control systems of pesticides residues in crops is planned official inspection of pesticides residues on the stage of the primary vegetable production of foodstuffs.

The present food on the market can contain residues of pesticides on level not to higher than obligatory values MRL. In the chance of the offence MRL follows the notification to Rapid Alert System for Food and Feed (RASFF).

The aim of work was the estimate short- and long-term exposure of consumers to the pesticide residues from fruits and vegetables (together 32 crops) proceeding from North-Eastern Poland.

Data concerning estimations of the risk one received on the ground findings of led official inspection in years 2005, 2006, 2007 in North-Eastern Poland. The Pesticide Residue Laboratory in Bialystok estimated intake pesticide residues by consumers for two age groups, ie small children (the mass of the body to 14 kg) and adult, using to this end new models of the British Pesticides Safety Directorate.

Obtained results show that the long-term exposure is low enough. For adult it does not top 10 %, and for children is lower than 40 % values of acceptable daily intake (ADI).

An acute exposure was calculated only for compounds exceeding MRL. The estimating short-term exposure in the chance adult imperceptibly tops 60 %, instead in the case of children does not exceed 80 % acute reference dose (ARfD).

The results show that fruit and vegetables proceeding from North-Eastern Poland are safe for children and adult consumers in long – as well as in short-term nutrition.

Keywords: pesticide residues, dietary exposure, crops

Pesticides are projected into such manner, that exert influence on basic processes in living organisms and can kill injurious organisms, or to serve the inspection of such organisms. Simultaneously it can cause undesirable negative results for other organisms

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[1] Institute of Plant Protection, Pesticide Residue Laboratory in Bialystok, ul. J. Chełmońskiego 22, 15–195 Białystok, Poland, phone 85 678 5470, fax 85 675 3419, email: B.Lozowicka@ior.poznan.pl

than of approach, for the human health. The society is accepted by in a manner possible connected threats with the usage of pesticides in consideration of connected with them economic advantages, because among other things pesticides contribute to the assurance of farming products of the high grade and after the moderate price. The healthy and safe food should be characterized suitable food value and with the possibly low content of the substance whose the presence can determine the health hazard, for example pesticides.

The control of pesticides residues on the stage of the primary production delivers given servants to the valuation of the risk of the exposure of the people health by intake in the diet residue of pesticides.

There exist two types of accepted levels of intake residues of pesticides in the food:

– acceptable daily intake (ADI) – the amount of a chemical that can be consumed every day for lifetime in the practical certainty, on the basis of all known facts, that no harm will result,

– acute reference dose (ARfD) – the amount of a chemical that can be consumed at one meal or on one day in the practical certainty, on the basis of all known facts, that no harm will result.

The best available food consumption data should be used for predictions of pesticide residue intake at the national level. Countries should use only average food consumption values if use of other values results in a hypothetical level of consumption that would not be attained in practice. In predicting the pesticide residue intake of identified subgroups relevant average food consumption data for such subgroups should be used. Subgroups, such as pregnant women, infants and children, high consumers and vegetarians, may require separate consideration [1]. Real levels of pesticides residues in these crops are obtained from controlled experimental fields and from controlled plant foodstuffs [2].

The risk of the exposure of the health of people remainders of pesticides is estimated, when:

– exceeded the Maximum Residue Levels (MRLs),
– detected the prohibited pesticide,
– residues was found in products about the high consumption.

The information concerning residues intake are combined with databases of found residues for the purpose of the estimation of both long-term, as well as short-term intake residue of pesticides by the diet. Estimating intake residues in the diet is then set against accepted safe levels (ADI and ARfD).

Material and methods

The data concerning residues for estimation of risk were received in 2005–2007 by the Pesticide Residue Laboratory in Bialystok of the official inspection of pesticides residues on the stage of the primary vegetable production of foodstuffs. The studies included 115 compounds in 710 fruits and vegetables samples originated from of North-Eastern Poland.

Results under limit of detection (LOD) of analytical methods used for intake calculations were taken as LOD values.

Values of ADI and ARfD are elaborated by European Food Safety Authority (EFSA) of European Union (EU) [3] or Federal Institute for Risk Assessment (BfR), Germany [4].

For consumer residues intake estimation were applied new model from Pesticides Safety Directorate (PSD) of the Department for Environment, British Food and Rural Affairs. Calculations were performed using a Chronic and Acute Consumer ver 1.1. with built-in consumption database for 10 groups of consumer [5].

Long-term risk was calculated as:

$$\mathrm{NEDI} = \sum \frac{\mathrm{F_i} \times \mathrm{RL_i} \times \mathrm{P_i}}{\mathrm{mean - body - weight}}$$

where: NEDI – National Estimated Daily Intake,
F_i – food consumption data
RL_i – residue level to the commodity,
P_i – correction value that takes into account the reduction or increase in residue which might occur on storage or processing.

The short-term risk was calculated for two cases [6]. Case 1, NESTI is calculated simply as the full portion consumption for the commodity multiplied by the highest residue level detected (after correction for processing or removal of non-edible portions). In this case short term risk was calculated according to the following formula:

$$\mathrm{NESTI} = \sum \frac{\mathrm{F} \times \mathrm{HR\text{-}P}}{\mathrm{mean - body - weight}}$$

where: NESTI – National Estimates of Short-Term Intake,
F – full portion consumption data for the commodity unit,
HR-P – the highest residue level detected after correction for processing or removal of non-edible portions.

More complex scenario (case 2) applies to a commodity for which the consumption at a single meal would consist of four or less discrete units of the commodity. Under these circumstances, the residue level, which is measured from a composite sample, has to be increased by a variability factor (v), which reflects the ratio of a high-level residue to the composite residue level (for which data are available). The value of v is likely to depend on the nature of the crop, the nature of the active ingredient and the method of pesticide application. In this case short term risk was calculated according to the following formula:

$$\mathrm{NESTI} = \sum \frac{(\mathrm{U} \times \mathrm{HR\text{-}P} \times \mathrm{v}) + (\{\mathrm{F} - \mathrm{U}\} \times \mathrm{HR\text{-}P})}{\mathrm{mean - body - weight}}$$

where: U – the weight of the first commodity unit (equivalent to the unit with the high residence level),
v – the "variability factor" (which allows for the fact that the measured highest residue level was determined for a composite sample that may have contained only a proportion of high residue units).

Table 1

Estimation of chronic dietary exposure to pesticide for apple in 2005–2007

Active substance	Average residue level [mg · kg^{-1}]	High level (97.5 percentile) of long term consumption by adults [kg · person^{-1} · day^{-1}]	High level (97.5 percentile) of long term consumption by toddlers [kg · person^{-1} · day^{-1}]	Acceptable daily intake (ADI) [mg · kg^{-1} body mass]	Intake			
					Adults [76 kg]		Toddlers [14.5 kg]	
					[mg · kg^{-1} body mass]	[% ADI]	[mg · kg^{-1} body mass]	[% ADI]
Acetamiprid	0.010261	0.2038	0.2156	0.07	0.000027515	0.039	0.000152569	0.218
Captan	0.048957	0.2038	0.2156	0.1	0.000131281	0.131	0.000727933	0.728
Carbendazim	0.020609	0.2038	0.2156	0.02	0.000055264	0.276	0.000306430	1.532
Chlorpyrifos	0.010087	0.2038	0.2156	0.01	0.000027049	0.270	0.000149983	1.500
Cyprodinil	0.011304	0.2038	0.2156	0.03	0.000030314	0.101	0.000168084	0.560
Diazinon	0.010087	0.2038	0.2156	0.005	0.000027049	0.541	0.000149983	3.000
Dimethoate	0.011130	0.2038	0.2156	0.001	0.000029847	2.985	0.000165498	16.550
Dithiocarbamates	0.078087	0.2038	0.2156	0.03	0.000209396	0.698	0.001161072	3.870
Flusilazole	0.010609	0.2038	0.2156	0.002	0.000028448	1.422	0.000157740	7.887
Pirimicarb	0.014522	0.2038	0.2156	0.035	0.000038941	0.111	0.000215923	0.617
Pyrimethanil	0.021652	0.2038	0.2156	0.17	0.000058062	0.034	0.000321945	0.189
Tolylfluanid	0.021043	0.2038	0.2156	0.1	0.000056430	0.056	0.000312895	0.313
Trifloxystrobin	0.010174	0.2038	0.2156	0.1	0.000027282	0.027	0.000151276	0.151
Total						6.7		37.1

Table 2

Estimation of chronic dietary exposure to pesticide for black currant 2005–2007

Active substance	Average residue level [mg · kg^{-1}]	High level (97.5 percentile) of long term consumption by adults [kg · person^{-1} · day^{-1}]	High level (97.5 percentile) of long term consumption by toddlers [kg · person^{-1} · day^{-1}]	Acceptable daily intake (ADI) [mg · kg^{-1} body mass]	Intake			
					Adults [76 kg]		Toddlers [14.5 kg]	
					[mg · kg^{-1} body mass]	[% ADI]	[mg · kg^{-1} body mass]	[% ADI]
Alpha-Cypermethrin	0.031429	0.0436	0.026	0.015	0.000018030	0.120	0.000056355	0.376
Bupirimate	0.010857	0.0436	0.026	0.05	0.000006229	0.012	0.000019468	0.039
Dithiocarbamates	0.051143	0.0436	0.026	0.03	0.000029340	0.098	0.000091704	0.306
Endosulfan	0.030000	0.0436	0.026	0.006	0.000017211	0.287	0.000053793	0.897
Fenazaquin	0.028286	0.0436	0.026	0.005	0.000016227	0.325	0.000050719	1.014
Fenitrothion	0.022857	0.0436	0.026	0.005	0.000013113	0.262	0.000040985	0.820
Flusilazole	0.021714	0.0436	0.026	0.002	0.000012457	0.623	0.000038936	1.947
Procymidone	0.035714	0.0436	0.026	0.025	0.000020489	0.082	0.000064039	0.256
Trifloxystrobin	0.010286	0.0436	0.026	0.1	0.000005901	0.006	0.000018443	0.018
Total						1.8		5.7

Table 3

Estimation of chronic dietary exposure to pesticide for strawberry in 2005–2007

Active substance	Average residue level [mg · kg^{-1}]	High level (97.5 percentile) of long term consumption by adults [kg · person^{-1} · day^{-1}]	High level (97.5 percentile) of long term consumption by toddlers [kg · person^{-1} · day^{-1}]	Acceptable daily intake (ADI) [mg · kg^{-1} body mass]	Intake			
					Adults [76 kg]		Toddlers [14.5 kg]	
					[mg · kg^{-1} body mass]	[% ADI]	[mg · kg^{-1} body mass]	[% ADI]
Cyprodinil	0.016964	0.0449	0.0289	0.03	0.000010022	0.033	0.000033812	0.113
Chlorpyrifos	0.010000	0.0449	0.0289	0.01	0.000005908	0.059	0.000019931	0.199
Dithiocarbamates	0.084643	0.0449	0.0289	0.03	0.000050006	0.167	0.000168702	0.562
Fenhexamide	0.054464	0.0449	0.0289	0.2	0.000032177	0.016	0.000108553	0.054
Fludioxonyl	0.021429	0.0449	0.0289	0.37	0.000012660	0.003	0.000042709	0.012
Folpet	0.030357	0.0449	0.0289	0.1	0.000017935	0.018	0.000060505	0.061
Iprodione	0.093571	0.0449	0.0289	0.06	0.000055281	0.092	0.000186498	0.311
Procymidone	0.042857	0.0449	0.0289	0.025	0.000025320	0.101	0.000085419	0.342
Pyrimethanil	0.017143	0.0449	0.0289	0.17	0.000010128	0.006	0.000034167	0.020
Tolylfluanid	0.030357	0.0449	0.0289	0.1	0.000017935	0.018	0.000060505	0.061
Total						0.5		1.7

Table 4

Estimation of chronic dietary exposure to pesticide for cherry in 2005–2007

Active substance	Average residue level [mg · kg^{-1}]	High level (97.5 percentile) of long term consumption by adults [kg · person^{-1} · day^{-1}]	High level (97.5 percentile) of long term consumption by toddlers [kg · person^{-1} · day^{-1}]	Acceptable daily intake (ADI) [mg · kg^{-1} body mass]	Intake			
					Adults [76 kg]		Toddlers [14.5 kg]	
					[mg · kg^{-1} body mass]	[% ADI]	[mg · kg^{-1} body mass]	[% ADI]
Alpha-Cypermethrin	0.030347	0.0358	0.0152	0.015	0.000014295	0.095	0.000031812	0.212
Bitertanol	0.050347	0.0358	0.0152	0.01	0.000023716	0.237	0.000052778	0.528
Captan	0.147708	0.0358	0.0152	0.1	0.000069578	0.070	0.000154839	0.155
Diazinon	0.010000	0.0358	0.0152	0.005	0.000004711	0.094	0.000010483	0.210
Dithiocarbamates	0.031111	0.0358	0.0152	0.03	0.000014655	0.049	0.000032613	0.109
Fenarimol	0.010764	0.0358	0.0152	0.01	0.000005070	0.051	0.000011284	0.113
Flusilazole	0.010625	0.0358	0.0152	0.002	0.000005005	0.250	0.000011138	0.557
Pirimicarb	0.021250	0.0358	0.0152	0.035	0.000010010	0.029	0.000022276	0.064
Total						0.9		1.9

Table 5

Estimation of acute dietary exposure of pesticides based on their highest residues in crops in 2005–2007 (case 1)

Active substance	Commodity	The highest residue level (HR) [mg · kg^{-1}]	Acute Reference Dose (ARfD) [mg · kg^{-1} body mass]	Full portion consumption data (97.5 percentile)		Intake			
						Adults [76 kg]		Toddlers [14.5 kg]	
				Adults [kg]	Toddlers [kg]	[mg · kg^{-1} body mass]	[% ARfD]	[mg · kg^{-1} body mass]	[% ARfD]
Carbendazim	Mushrooms	0.45	0.02	0.0304	0.0153	0.00072	3.6	0.00132	6.6
Alpha-Cypermethrin	Black currant	0.08	0.04	0.0436	0.026	0.00013	0.3	0.00029	0.7
Endosulfan	Black currant	0.03	0.02	0.0436	0.026	0.00005	0.2	0.00011	0.5
Fenitrothion	Black currant	0.07	0.013	0.0436	0.026	0.00011	0.9	0.00025	1.9
Flusilazole	Black currant	0.29	0.005	0.0436	0.026	0.00046	9.2	0.00104	20.9
Procymidone	Black currant	0.57	0.035	0.0436	0.026	0.00090	2.6	0.00205	5.9

Table 6

Estimation of acute dietary exposure of pesticides based on their highest residues in crops in 2005–2007 (case 2)

Active substance	Commodity	The highest residue level (HR) [$mg \cdot kg^{-1}$]	Acute Reference Dose (ARfD) [$mg \cdot kg^{-1}$ body mass]	Variability factor (v)	The weight of first commodity unit (U) [kg]	Full portion consumption data (97.5 percentile)		Intake			
								Adults [76 kg]		Toddlers [14.5 kg]	
						Adults [kg]	Toddlers [kg]	[$mg \cdot kg^{-1}$ body mass]	[% ARfD]	[$mg \cdot kg^{-1}$ body mass]	[% ARfD]
Cyprodinil	Apple	0.09	0.03	7	0.112	0.2038	0.2156	0.00045	1.5	0.00172	5.7
Dimethoate	Apple	0.1	0.01	7	0.112	0.2038	0.2156	0.00150	15.0	0.00720	72.0
Pyrimethanil	Apple	0.48	0.2	7	0.112	0.2038	0.2156	0.00718	3.6	0.03458	17.3
Tolylfluanid	Apple	0.29	0.25	7	0.112	0.2038	0.2156	0.00434	1.7	0.02089	8.4
Chlorpyrifos	Broccoli	0.21	0.1	5	0.68	0.0491	0.0248	0.00270	2.7	0.00440	4.4
Dichlofluanid	Lettuce	18.7	0.3	5	0.558	0.0471	0.0124	0.18454	61.5	0.22569	75.2
Diazinon	Lettuce	0.27	0.025	5	0.558	0.0471	0.0124	0.00266	10.7	0.00326	13.0

Results and discussion

In Table 1 has shown chronic dietary exposure estimation for people consuming all detected pesticide residues in 2005–2007 in 115 apple samples – the fruit of the highest consumption in Poland. Table 2 shows the same data for 35 samples of black currant, the fruit where the most often are observed MRLs exceeding and inconsistent pesticide usage [7]. Table 3 and 4 shows the data for samples of strawberry and cherry, the fruit where the most often residues of pesticide are found.

The data show the chronic dietary exposure is pretty low. For adults it does not exceed 10 %, and for toddlers it is lower than 40 % of ADI acceptable level despite of common addition of all individual exposures, that usually results with obtained data overestimation. An estimated long-term exposure for another products was significantly more lower than these presented data.

An acute exposure was calculated only for compounds exceeding MRL [7] and inconsistent pesticide usage. The maximum exposure for adults exceeded 60 % of ARfD, while for toddlers was lower than 80 % of ARfD allowed value (Table 5 and 6).

The presented data show that fruits and vegetables from North-Eastern Poland are safe in long-term as well as in short-term for toddlers and adults.

Conclusions

Chronic dietary exposure is pretty low, for adults it does not exceed 10 %, and for toddlers it is lower than 40 % of ADI. An acute exposure exceeded 60 % of ARfD, while for toddlers was lower than 80 % of ARfD allowed value.

Fruits and vegetables from North-Eastern Poland are safe for small and adult consumers when consumed both occasionally and permanently. However studies on pesticide residues should be still developed and should include more active substances and various species of vegetables and fruits.

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ZAGROŻENIE ZDROWIA KONSUMENTÓW POZOSTAŁOŚCIAMI PESTYCYDÓW Z PŁODÓW ROLNYCH PÓŁNOCNO-WSCHODNIEJ POLSKI

Instytut Ochrony Roślin – Państwowy Instytut Badawczy
Labolatorium Badania Pozostałości Środków Ochrony Roślin w Białymstoku

Abstrakt: Najwyższe dopuszczalne poziomy pozostałości pestycydów (NDP) w środkach spożywczych, jako obowiązujące wartości normatywne ukazały się w polskim ustawodawstwie dotyczących żywności w 1993 r. Wśród obecnie obowiązujących wartości NDP rozróżnia się wartości implementowane z Dyrektyw Unii Europejskiej (MRL) oraz tzw. narodowe NDP (Rozporządzenie Ministra Zdrowia z dnia 16 maja 2007 r. DzU nr 119, poz. 817). Jednym z systemów kontroli pozostałości pestycydów w płodach rolnych jest urzędowy monitoring na etapie pierwotnej produkcji rolnej żywności pochodzenia roślinnego.

Żywność obecna na rynku może zawierać pozostałości pestycydów na poziomie nie wyższym niż obowiązujące wartości NDP. W przypadku przekroczenia NDP następuje zgłoszenie do Systemu Wczesnego Ostrzegania o Niebezpiecznych Produktach Żywnościowych i Środkach Żywienia Zwierząt (RASFF).

Celem badań była ocena krótko- i długoterminowego pobrania pozostałości pestycydów z owoców i warzyw (łącznie 32 uprawy) pochodzących z północno-wschodniej Polski.

Do oceny ryzyka wykorzystano dane uzyskane z urzędowej kontroli w zakresie pozostałości pestycydów w owocach i warzywach w latach 2005–2007 w północno-wschodniej Polsce. Laboratorium Badania Pozostałości Środków Ochrony Roślin IOR w Białymstoku oceniło pobranie pozostałości pestycydów przez konsumentów dla dwóch grup wiekowych, tj. małych dzieci (masa ciała do 14 kg) i dorosłych, wykorzystując do tego celu nowe modele brytyjskiego Urzędu Bezpieczeństwa Pestycydów.

Uzyskane wyniki wskazują, iż długoterminowe narażenie jest dość małe. Dla dorosłych nie przewyższa 10 %, a dla dzieci jest mniejsze niż 40 % wartości bezpiecznego dziennego pobrania (ADI – *Acceptable Daily Intake*).

Narażenie jednorazowe wyznaczono dla przypadków, w których stwierdzono przekroczenia najwyższych dopuszczalnych poziomów pozostałości (NDP) lub zastosowanie zabronionych preparatów. Oceniono narażenie krótkoterminowe w przypadku dorosłych było nieznacznie większe od 60 %, natomiast w przypadku dzieci nie przekraczało 80% ostrej dawki referencyjnej (ARfD – *Acute Reference Dose*).

Przeprowadzone badania wykazały, że owoce i warzywa pochodzące z północno-wschodniej Polski są bezpieczne dla dzieci i dorosłych konsumentów zarówno w trakcie krótkoterminowego pobrania pestycydu z żywnością, jak i w długim okresie spożycia.

Słowa kluczowe: pozostałości pestycydów, narażenie konsumentów, płody rolne

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Edward MAJCHERCZAK[1] and Wojciech KOZERA[1]

CROP YIELD AND CHEMICAL COMPOSITION OF THE SPRING TRITICALE AND OAT GRAINS FERTILISED WITH ORGANIC WASTE AND MANURE

PLONOWANIE ORAZ SKŁAD CHEMICZNY ZIARNA PSZENŻYTA JAREGO I OWSA NAWOŻONYCH ODPADAMI ORGANICZNYMI I OBORNIKIEM

Abstract: This research was conducted in the years 2004–2005 on Luvisols of the 6th class in a system of randomized blocks as one-factor experiment with three replications. The tested factor was a type of the applied organic matter (manure, fowl litter and conditioned waste from poultry abattoir), the doses of which were determined so that the amount of nitrogen introduced into soil would not exceed 170 N kg · ha^{-1}. The influence of the applied fertilisation on the crop yield and chemical composition of the cultivated plants was assessed.

The experiment carried out showed that the use of conditioned waste significantly increased the grain crop yields of spring triticale and oat with reference to the control. The grain of those plants reaped from the objects where a conditioned waste from poultry abattoir was applied contained the lower total nitrogen amount with reference with the control. However, the crop yield of total protein, which is dependent on the amount of grain crop yield and the grain total nitrogen content was clearly higher after using the conditioned waste, compared with the objects only with mineral fertilizers application.

Keywords: spring triticale, oat, manure, organic waste

Organic waste may become a valuable source of macro- and microelements for plants and play an important role in a balance of organic substance [1]. Fowl litter as a waste product from poultry farms and the conditioned waste from poultry hatcheries may be used as alternative fertilizers together with the manure [2, 3]. Their chemical composition indicates that they are abundant in mineral constituents required for the plant growth and development [4, 5]. Organic substances are mostly used to cultivate root crops, however, according to the Act on Fertilisers and Fertilisation [6], their appropriate use may be a problem in the vicinity of large livestock raising farms.

The aim of this study was to compare the effect of manure, fowl litter and conditioned waste from poultry abattoir on the crop yield of selected plants cultivated in light soil.

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[1] Department of Agricultural Chemistry, University of Technology and Life Sciences, ul. Seminaryjna 5, 85–326 Bydgoszcz, Poland, phone 52 374 9104, fax 52 374 9103, email: majcher@utp.edu.pl, kozera@utp.edu.pl

Material and methods

The field experiment was carried out in 2004–2005 on Luvisols of the 6th class, a very poor rye soil complex, originated from glacial sands of Baltic Glaciations. Soil was characterized by acid reaction, low content of available forms of phosphorus and potassium and low abundance in available forms of magnesium. The investigation was realised as one-factor experiment in a system of randomised blocks with three replications, the tested plot area was 40 m^2. The tested factor was a type of organic matter and its doses were determined so that the amount of nitrogen introduced into soil would not exceed 170 $kg\ N \cdot ha^{-1}$. A spring triticale was the test plant in the first year of the experiment and oat was in the second year.

A scheme of the field experiment included seven fertilised objects (plots):

K_0 – the control (mineral fertilisation),
K_1 – cattle stable manure applied every year,
K_2 – cattle stable manure applied once per every two years,
K_3 – fowl litter used every year,
K_4 – fowl litter applied once per every two years,
K_5 – conditioned waste from poultry abattoir, applied once per year,
K_6 – conditioned waste from poultry abattoir, applied once per every two years.

A grain crop yield of the test plants was determined at the harvest time. The content of total nitrogen in grain was determined by using Kjeldahl's method, phosphorus – colorimetrically, potassium and calcium by the method of flame photometry, and magnesium by using atomic absorption spectrometry (AAS). Additionally, a crop yield of total protein was calculated.

The climatic conditions were registered during the experiment (Table 1).

Table 1

Monthly total precipitation and mean air temperatures in plant vegetation period

Year	Month						Sum III–VIII
	III	IV	V	VI	VII	VII	
Precipitation [mm]							
2004	35.8	32.1	54.4	39.6	53.5	138.7	354.1
2005	22.5	34.8	82.6	30.5	33.6	43.4	247.4
Multi-year	31.8	27.5	58.7	48.3	83.7	60.8	310.8
Temperature [°C]							Mean
2004	2.9	7.5	11.3	14.7	16.4	17.9	8.8
2005	–0.4	7.4	12.2	14.9	19.4	16.3	8.7
Multi-year	2.2	7.8	13.2	16.1	18.0	18.2	9.4

The obtained test results were statistically worked out by using variance analysis at the level of significance $\alpha = 0.05$ and the differences were estimated by Tukey's test.

Results

The use of organic substances resulted in the increase in the grain crop yield of spring triticale and oat (Table 2) by 0.78 Mg · ha^{-1} and 0.48 Mg · ha^{-1} on average, respectively, with reference to the control.

It was found that in the second year of the field experiment the oat grain crop yields on the objects K_2, K_4 and K_6 were lower by approx 13.7 % with reference to the control and those reductions were statistically proven. It is worth noticing that differences between the achieved grain crop yields of the cultivated plants are not statistically significant considering a type of the applied organic material.

Fertilisation with manure and organic waste reduced total nitrogen contents in the grain of cultivated plants (Table 2). Statistically proven levels of these reductions were indicated for the objects where organic material was used in the year of the experiment, and they amount to 2.8–4.3 g N · kg^{-1} for spring triticale grain and 1.2–1.9 g N · kg^{-1} for oat grain.

The calculated crop yields of total protein in the grain of spring triticale and oat fertilised with organic matter are statistically higher in comparison with the control (Table 2). The increases in the spring triticale total protein varied from 86.5 kg · ha^{-1} in object K_2 to 102.9 kg · ha^{-1} in object K_5 with reference to the control and those for oat ranged from 36.2 kg · ha^{-1} to 63.8 kg · ha^{-1}. The total protein crop yields of the tested plants fertilised with organic substances once per two years were distinctly lower by 21.3 kg · ha^{-1} with reference to the fertilised objects, however these values were not statistically proven.

Fertilisation applied in the experiment modified the content of total phosphorus in spring triticale and oat grain varying within the range from 3.77 to 4.00 g P · kg^{-1} and from 3.76 to 3.95 g P · kg^{-1}, respectively. However, the achieved differences were not statistically proven.

Fertilisation with manure or fowl litter resulted in statistically significant increase in potassium content in spring triticale grain by 0.84 g K · kg^{-1} on average with reference to the control. A statistically proven increase in the amount of this element by 0.85 g K · kg^{-1} on average was also achieved in oat grain fertilised annually with manure or fowl litter. Using conditioned waste from poultry abattoir decreased potassium content in both triticale and oat grain with reference to the control, however, these values were not statistically proven.

The research carried out showed that fertilisation with conditioned waste from poultry abattoir resulted in statistically proven decrease in calcium content in spring triticale grain by 14.1 % on average with reference to the object not fertilized with organic substances. The triticale grain from the object where manure or fowl litter was applied contained more calcium in grain, on average by 14.1 % higher with reference to the control. No statistically proven difference in calcium contents in oat grain was found under the effect of the applied fertilisation and its content ranged from 0.48 to 0.55 g Ca · kg^{-1}.

A mean content of magnesium in spring triticale grain amounted to 1.48 g Mg · kg^{-1} and was not significantly modified by the tested factors. At the same time the grain of oat fertilized with organic matter contained more magnesium with reference to the

Table 2

Yield and chemical composition of grain spring triticale and oat

Parameter		Plant	Fertilizations objects							Mean	LSD
			K_0	K_1	K_2	K_3	K_4	K_5	K_6		
Grain yield [Mg · ha^{-1}]		triticale	1.04	1.86	1.83	1.78	1.81	1.84	1.82	1.71	0.147
		oat	1.15	1.79	1.53	1.71	1.49	1.75	1.50	1.56	0.138
N-total [g · kg^{-1}]		triticale	27.0	22.7	22.9	23.6	23.3	24.2	24.1	24.0	2.45
		oat	20.5	18.6	19.6	18.9	19.7	19.3	19.9	19.5	1.18
Protein yield [kg · ha^{-1}]		triticale	175.4	263.9	261.9	262.6	263.6	278.3	274.1	254.3	32.01
		oat	147.3	208.1	187.4	202.0	183.5	211.1	186.6	189.4	27.61
P	[g · kg^{-1}]	triticale	4.00	3.77	3.81	3.78	3.80	3.95	3.89	3.86	n. s.
		oat	3.95	3.80	3.76	3.77	3.81	3.89	3.88	3.83	n. s.
K		triticale	4.55	5.31	5.33	5.47	5.44	4.12	4.09	4.90	0.637
		oat	5.11	5.95	5.44	5.96	5.59	4.97	4.61	5.38	0.531
Ca		triticale	0.32	0.38	0.36	0.35	0.37	0.27	0.28	0.33	0.029
		oat	0.51	0.55	0.54	0.53	0.52	0.49	0.48	0.52	n. s.
Mg		triticale	1.49	1.48	1.47	1.48	1.47	1.47	1.49	1.48	n. s.
		oat	1.28	1.43	1.35	1.44	1.34	1.36	1.33	1.36	0.125

control. However, the achieved differences were statistically proven only for the grain obtained from the object annually fertilized with manure or fowl litter and were: 0.15 and 0.16 g Mg $\cdot$ kg^{-1}, respectively, with reference to the control.

Discussion

In the subject literature, the opinion prevails that fertilisation with organic substances affects the increase in the grain crop yield of cereal plants [7–9]. The results of Authors research confirm this opinion and the achieved growths in grain crop yield range from 29.6 % to 78.8 %. Similar increases in grain crop yields (by 60 %) were obtained by Stepien and Mercik [4] who applied feather meal cultivating spring triticale. Low crop yields of spring triticale 1.71 Mg $\cdot$ ha^{-1} and oat 1.56 Mg $\cdot$ ha^{-1} in our own research resulted from extremely low precipitation during plant vegetation period and a type of soil where the field experiment was carried out (Table 1).

Fertilisation with manure or other organic matter resulted in increase in the total nitrogen contents in the grain of cereal plants [5, 10, 11]. In our research it was found that the use of organic matter for cereal cultivation is to the detriment of the total nitrogen accumulation in grain. It probably resulted from a low amount of precipitation in the years of conducting the field experiment, which is crucial for the effectiveness of the applied fertilisation.

The increase in both grain crop yield and total nitrogen contents is brought about a considerable increase in total protein under the effect of applying organic matter [5, 10]. Using mineral and natural fertilization, Cwojdziński and Nowak [12] achieved the increase in the total protein crop yield by 181 % for spring barley and by 157 % for spring wheat; in our own research the growths in this crop yield ranged from 24.6 % to 58.7 %. Such a low increase in total protein of spring triticale and oat is a consequence of significant reduction of its content in the grain of these cereals.

The research by Stepien and Mercik [4] proves that applying feather meal induces the growth in contents of potassium, calcium and magnesium in spring triticale grain and does not modify the content of total phosphorus. The results of our own research showed that the use of conditioned waste from poultry abattoir significantly reduced only the amount of calcium in spring triticale grain. Differences in the results obtained may account for different granulation rate of the applied waste, which is important for the rate of its decay in soil. Rabikowska [10] demonstrated that fertilisation with manure increased the content of phosphorus in the grain of maize, but had no effect on calcium content. The research by Szulc [13] argues that mineral-natural fertilisation does not increase magnesium content in cereal grain. Our own research indicated that fertilization with manure or fowl litter increased the amount of: potassium in the grain of spring triticale and oat, calcium in spring triticale grain, and magnesium in oat grain. The growths of potassium contents in the achieved crop yield do not confirm the research made by Sadej and Mazur [7]. The diversity observed in the results of the research is probably a consequence of very unfavourable weather conditions so characteristic of the years 2004–2005, when the experiments were performed.

Conclusions

1. After applying manure, fowl litter or conditioned waste from poultry abattoir, a significant growth in the grain crop yields of spring triticale and oat as well as total protein content in their grains was observed. It indicates the possibility of usage these products in cereal fertilization.

2. Using organic substances in the fertilisation of triticale and oat reduced the total nitrogen content in the grain of these plants.

3. The research showed that natural fertilisation increased: potassium content in the spring triticale and oat grains, calcium in triticale grain, and magnesium in oat grain.

4. Fertilisation with conditioned waste from poultry abattoir lowered calcium content in spring triticale grain.

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PLONOWANIE ORAZ SKŁAD CHEMICZNY ZIARNA PSZENŻYTA JAREGO I OWSA NAWOŻONYCH ODPADAMI ORGANICZNYMI I OBORNIKIEM

Katedra Chemii Rolnej
Uniwersytet Technologiczno-Przyrodniczy w Bydgoszczy

Abstrakt: Badania przeprowadzono w latach 2004–2005 na glebie płowej, zaliczanej do VI klasy. Eksperyment realizowano jako doświadczenie jednoczynnikowe w trzech powtórzeniach metodą losowanych bloków. Czynnikiem badawczym był rodzaj zastosowanej masy organicznej (obornik, pomiot ptasi i kondycjonowany odpad z ubojni drobiu), a jej dawki określono tak, aby ilość wprowadzonego azotu do gleby nie przekroczyła 170 kg N $\cdot$ ha^{-1}. Oceniano wpływ zastosowanego nawożenia na plon i skład chemiczny uprawianych roślin.

Przeprowadzone badania wykazały, że stosowanie kondycjonowanego odpadu powodowało znaczący wzrost plonów ziarna pszenżyta jarego i owsa w stosunku do obiektu kontrolnego. Ziarno roślin pozyskanych z obiektów, na których stosowano kondycjonowany odpad z ubojni drobiu, zawierało mniej azotu ogólnego w odniesieniu do kontroli. Jednakże plon białka ogólnego, który zależy od ilości plonu ziarna i zawartości w nim azotu ogólnego, był wyraźnie większy po zastosowaniu kondycjonowanego odpadu w porównaniu z uzyskanym z obiektów nawożonych tylko nawozami mineralnymi.

Słowa kluczowe: pszenżyto jare, owies, obornik, odpady organiczne

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Zbigniew MAZUR[1]

EFFECT OF FARM MANURE APPLICATION AND NPK FERTILIZATION ON CARBON DIOXIDE CONCENTRATION IN SOIL AIR

WPŁYW NAWOŻENIA OBORNIKIEM I NPK NA ZAWARTOŚĆ DITLENKU WĘGLA W POWIETRZU GLEBOWYM

Abstract: The results of measurements of carbon dioxide concentration in soil air under conditions of an exact field experiment are presented. Compared with CO_2 content in the control plot, manure application combined with NPK fertilization caused an increase in CO_2 levels by 0.06 % and 0.04 % by volume, while manure application alone – by only 0.02 %. Measurements were performed for 12 weeks, from the end of June to the middle of September 1999. Throughout that period, average CO_2 concentration decreased in all treatments, from 0.62 % to 0.16 % by volume.

Keywords: fertilization, carbon dioxide, soil air

Carbon dioxide concentration in soil air is one of the indicators of soil organic matter mineralization. Few studies have investigated this issue to date. Therefore, the objective of the present study was to determine the CO_2 content of soil air in an exact field experiment with potato grown under different fertilizing conditions.

Materials and methods

Carbon dioxide concentration in soil air was studied based on the results of a field experiment conducted within the framework of the project "Comparison of the Ecological Effects of Mineral and Organic Fertilization", supported financially by the State Committee for Scientific Research. The above results have already been published [1], and the current study focused on fluctuations in the CO_2 content of soil air as

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[1] Department of Environmental Chemistry, University of Warmia and Mazury in Olsztyn, pl. Łódzki 4, 10–718 Olsztyn, Poland, phone 89 523 35 42, email: zbigniew.mazur@uwm.edu.pl

dependent on fertilization levels (Table 1). Potatoes, 'Mila' cv., were grown in the year of the study. Farmyard manure, phosphorus and potassium fertilizers and 1/3 of the nitrogen rate were ploughed-in to a depth of 15 cm in the spring. The second and third rate of nitrogen was applied as top-dressing. Carbon dioxide concentration was measured at two-week intervals, between 26 June and 17 September 1999, using plastic tubes with perforated lower ends. The tubes were inserted into soil in each plot so that the lower perforated end was placed at a depth of 15–30 cm. The tubes were closed at the upper end so as to prevent the exchange of soil air with atmospheric air. Measurements were performed with the use of an Air TECH 2060-PA.

Results

Mean values, including the minimum and maximum carbon dioxide concentration, were determined based on a total of 28 individual measurements performed in each plot. The effect of the applied fertilizers on the CO2 content of soil air is presented in Table 1.

Table 1

Effect of fertilization on carbon dioxide concentration in soil air

Fertilization	CO_2 concentration [% by volume*]			V** [%]
	minimum*	maximum*	mean	
No fertilization	0.25	0.42	0.34	19.1
1/3 manure+1/3 NPK	0.28	0.53	0.40	22.3
1/3 manure+2/3 NPK	0.30	0.45	0.38	17.5
Manure	0.29	0.42	0.36	21.0
NPK	0.24	0.41	0.33	18.2
Mean	0.27	0.45	0.36	19.6
$LSD_{0.05}$			0.03	

* Repetitions of individual measurements; ** V – Variation coefficient.

The obtained data indicate that manure application combined with NPK fertilization caused an increase in CO_2 content, ranging from 0.02 to 0.06 % by volume. CO_2 concentration was slightly lower in the manure treatment than in the manure + + NPK treatments. NPK fertilization alone had no significant effect on the CO_2 content of soil air. Manure application reduced the differences between the minimum and maximum CO_2 content, in comparison with the manure + NPK and NPK treatments.

Individual measurements revealed considerable changes in CO_2 concentration in soil air (Table 2).

Over the period from the third week of June to the middle of September, ie during 12 weeks, the CO_2 content of soil air decreased 3.9-fold, ie from 0.62 % to 0.16 % by volume. The decrease in the minimum CO_2 concentration was smaller than the drop in the maximum CO_2 concentration (2.7-fold vs 5.0-fold). However, this decrease was not consistent and gradual – the most significant differences were noted between 1st and 2nd week, and between 6th and 8th week, which resulted primarily from a lower rate of soil organic matter mineralization.

Table 2

Carbon dioxide concentration in soil air during the potato growing season*

Weeks*	Mean CO_2 concentration [% by volume] (mean values of treatments)		
	minimum	maximum	mean
1	0.38	0.85	0.62
2	0.22	0.39	0.31
4	0.39	0.60	0.50
6	0.36	0.65	0.52
8	0.22	0.28	0.25
10	0.17	0.19	0.18
12	0.14	0.17	0.16
Mean	0.26	0.44	0.35
$LSD_{0.05}$			0.06

* From 27 June to 17 September 1999.

The dynamics of the decrease in the CO_2 content of soil air during the potato growing season was determined based on a regression equation (Fig. 1).

The value of the coefficient of determination ($R^2 = 0.62$) confirms the significant decrease in CO_2 concentration in soil air during the potato growing season. This decrease resulted from a lower rate of soil organic matter mineralization related to the low content of easily biodegradable organic compounds.

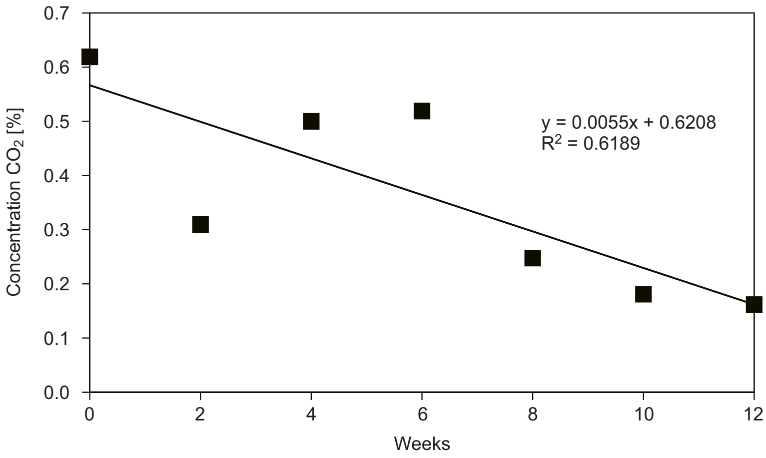

Fig. 1. Dynamics of CO_2 concentration in soil during the potato growing season (mean values of treatments)

Discussion

The carbon dioxide content of soil air is dependent on the quantity and quality of soil organic matter but also on the aerobic biological activity of soil, since under aerobic conditions carbon contained in SOM is oxidized to CO_2. Mineralization processes are affected by soil texture, which has been documented by numerous authors [2, 3]. Those processes are also determined by the composition of organic compounds which undergo breakdown and degradation at different rates. Previous studies usually involved compounds that are easily mineralized. Koter and Mazur [4] and Mazur and Raczyński [5] demonstrated that the rate of glycose mineralization and the kinetics of $C^{14}O_2$ evolution during the degradation of C^{14}-labeled amino acids were very fast and depended on soil type. In field investigations, the processes of mineralization and organic matter transformation are determined based on the humus-forming value [6, 7]. Such investigations, followed by CO_2 measurements, provide interesting results, which has been confirmed in long-term fertilization experiments [8]. The results of short-term fertilization trials [4] can also enrich the body of professional literature in this subject area. In the present study the application of manure and manure + NPK contributed to a rise in the CO_2 content of soil air, ranging from 5.9 % to 17.6 % in comparison with non-fertilized treatments. One may conclude that gas diffusion increases CO_2 concentration in the lower atmospheric layer, thus it may affect photosynthesis and crop yielding.

Conclusions

1. Manure application contributed to a lower increase in the CO_2 content of soil air than the joint application of manure + NPK.
2. During the potato growing season (end of June to mid-September), CO_2 concentration in soil air dropped on average from 0.62 % to 0.16 % by volume.

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WPŁYW NAWOŻENIA OBORNIKIEM I NPK NA ZAWARTOŚĆ DITLENKU WĘGLA W POWIETRZU GLEBOWYM

Katedra Chemii Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: W pracy zamieszczono wyniki oznaczenia stężenia ditlenku węgla w powietrzu glebowym w warunkach ścisłego doświadczenia polowego. W stosunku do zawartości CO_2 w powietrzu glebowym w obiekcie kontrolnym, nawożenie obornikiem i NPK spowodowało wzrost stężenia CO_2 o 0,06 % i 0,04 % obj., a samym obornikiem tylko o 0,02 %. Pomiary prowadzono przez 12 tygodni od końca czerwca do połowy września. W ciągu tego okresu średnia zawartość CO_2 z wszystkich obiektów zmniejszyła się z 0,62 % do 0,16 % objętości.

Słowa kluczowe: nawożenie, dwutlenek węgla, powietrze glebowe

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Paweł MUSZYŃSKI[1]

SORPTION OF TRITON X-100 IN SOILS WITH VARIOUS GRAIN SIZE COMPOSITIONS: KINETICS, EFFECT OF pH, ELECTROLYTE AND TEMPERATURE

SORPCJA TRITONU X-100 W GLEBACH O RÓŻNYM UZIARNIENIU: KINETYKA, WPŁYW pH, ELEKTROLITU I TEMPERATURY

Abstract: A study was conducted on the sorption of the surfactant Triton X-100, with a static method, through shaking of 2 g of soil (Albic Luvisols, Haplic Luvisols, Haplic Cambisols) in 10 cm^3 of solution during 24 hours. The kinetics was also studied of the process and the efficiency of sorption of triton X-100 from solutions with different values (1–12) of pH, in the presence of electrolytes: KCl, NH_4Cl and $CaCl_2$, and at temperatures of 20, 25, 30, 35 and 50 ^{o}C. Experimental results showed good agreement with results calculated from the Langmuir's equation and from a pseudo quadratic equation of kinetics. In the loamy soil, sorption of TX-100 increased in a nearly linear manner within the whole range of concentrations studied, while in the loess and sandy soils it had a linear course in the range of low initial concentrations. A high rate of sorption was found within the initial 30 min of TX-100 contact with the soils, following which the sorption increased more slowly and to a lesser degree. The value of pH had no effect on the sorption of the surfactant from solution with concentration of 250 mg · dm^{-3}. At concentrations of 1000 and 2000 mg · dm^{-3} significantly higher sorption was observed for solutions with pH = 1, in all of the soils under study, and from solution with pH = 12 – in the loess and sandy soils. The presence of electrolyte caused an increase in triton sorption, but in a degree dependent on the type of electrolyte and on the soil properties, and on the concentration of the surfactant. A slight effect of temperature on the sorption of TX-100 in the soils was observed.

Keywords: triton X-100, sorption, kinetics, soil

Surfactants, or surface-active agents, are the basic components of cleaning agents, emulsions, and foaming agents. Due to their capacity for reducing surface tension, they are extensively used in various branches of industry, in construction, and in the production of pharmaceuticals, paints, and pesticides. Uncontrolled disposal of sewage from households and industry, with simultaneous mass-scale use of surfactants, causes that more and more of those substances penetrate to waters and soils [1, 2].

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[1] Faculty of Chemistry, University of Life Sciences, ul. Akademicka 15, 20–950 Lublin, Poland, phone 81 445 65 56.

Surfactants are noxious compounds that at high concentrations may constitute a hazard to human health and have a toxic effect for aquatic organisms. Certain surfactants have also an effect on the sorption, mobility and degradation of many dangerous compounds, eg pesticides, or chloric derivatives of hydrocarbons [3].

Processes of sorption of surfactants in soils are not known in depth. This is due, among other things, to the specific structure of surfactants that are composed of a non-polar part (hydrophobic) and a polar part, with ionic (cation and anion surfactants) or dipole (non-ionic surfactants) character.

It is commonly known that sorption of non-ionic surfactants shows a relation with their structure, ie with the number of oxyethylene groups and the length of hydrocarbon chain [4]. Also in studies a relation has been observed on the level of sorption of the compounds with the content of organic carbon, clay minerals, and Fe and Al oxides in soils [5, 6].

The objective of this study was to acquire knowledge on the course of sorption of a non-ionic surfactant, Triton X-100, in three soils – Albic Luvisols, Haplic Luvisols, Haplic Cambisols – in connection with the duration of the surfactant – soil contact, pH of solution, presence of electrolyte, and temperature.

Material and methods

Soil samples for the study were taken from the A_p horizon of a grey-brown podzolic soil with grain size composition of weakly-loamy silty sand (Albic Luvisols), grey-brown podzolic soil developed from loess, with grain size composition of clay silt (Haplic Luvisols), and brown soil developed from boulder loam, with grain size composition of heavy loam (Haplic Cambisols) (acc. to Polish Society of Soil Science), further referred to in this report, due to the character of the parent rock, as a sandy soil, a loess soil and a loamy soil. The soil samples were air-dried, screened through a sieve with 1 mm mesh, and averaged.

The basic physicochemical properties of the sandy, loess and loamy soils were as follows: grain size composition (fraction: share): 1.0–0.1 mm – 80, 1, 29 %; 0.1–0.02 mm – 14, 63, 19 %; 0.02–0.002 mm – 2, 27, 34 %; < 0.002 mm: 4, 9, 18 %; pH in 1 mol $KCl \cdot dm^{-3}$ – 3.9, 4.3, 5.6; organic carbon content – 5.0, 21.3, 17 $g \cdot kg^{-1}$; specific surface area – 8.67, 20.05, 49.09 $m^2 \cdot g^{-1}$; hydrolytic acidity (H_h) – 35.8, 41.7, 9.2 mmol $H^+ \cdot kg^{-1}$; sum of exchangeable bases (S) – 0, 30, 332.4 mmol(+) $\cdot kg^{-1}$; the sorptive capacity – 35.8, 71.7, 341.6 mmol(+) $\cdot kg^{-1}$.

Grain size composition was determined with the Cassagrande method as modified by Prószyński, organic carbon content with the Tiurin method, pH in 1 mol $KCl \cdot dm^{-3}$ – electrometrically, specific surface area with the method of water vapour adsorption, hydrolytic acidity acc. to procedure PB-38 and sum of exchangeable cations acc. to procedure PN-R-04027:1997 and sorptive capacity as sum H_h and S.

Triton X-100 (abbreviation TX-100) was used in the study, produced by Sigma-Aldrich (Germany), with the following parameters: mean molar mass 628 $g \cdot mol^{-1}$, mean number of oxyethylene groups 9.5, CMC (*critical micelle concentration*) 167 $mg \cdot dm^{-3}$ [7]. Sorption was conducted with the static method: 2 g of soil were shaken in 10 cm^3 of Triton solutions with concentrations of 50–2000 $mg \cdot dm^{-3}$ for 24 h. Soil suspension was centrifuged at 4000 rpm for 25 min. In the obtained solutions, after suitable dilution, intensity of emission was measured on the fluorescence spectrophotometer Varian Cary Eclipse (λ_{Ex} = 275 nm, λ_{Em} = 302 nm), and then Triton concentration was read from the calibration curve. Determinations of sorption were conducted in water solutions solutions with pH in the range of 1–12, in 0.1 $mol \cdot dm^{-3}$ solutions of KCl, NH_4Cl and $CaCl_2$, at temperatures from 20 to 50 ^oC and in the time interval from 5 to 2880 min. In studies of sorption in the presence of electrolyte the concentrations of TX-100 solutions were from 50 to 2000 $mg \cdot dm^{-3}$. In the remaining experiments the solutions used had concentrations of 250, 750, 1000 and 2000 $mg \cdot dm^{-3}$. The amount of sorbed Triton (q_e, [$mg \cdot kg^{-1}$]) was calculated from the formula:

$$q_e = (C_{in} - C_{eq}) \cdot V/m \qquad (1)$$

where: C_{in} and C_{eq} – the initial and equivalent concentrations of triton [$mg \cdot dm^{-3}$],
V – volume of solution [dm^3],
m – mass of soil [kg].

For the description of relations between the sorbed amounts of TX-100 and the equivalent concentration in solution the Langmuir isotherm was applied. The linear form of the Langmuir isotherm is represented by the following equation:

$$C_{eq}/q_e = 1/q_L \cdot K_L + C_{eq}/q_L \qquad (2)$$

where: q_e – the amount of triton sorbed by unit mass of soil [$mg \cdot kg^{-1}$],
C_{eq} – equivalent concentration of Triton [$mg \cdot dm^{-3}$],
q_L – the amount of triton sorbed by unit mass of soil required to cover the sorptive surface with a monolayer [$mg \cdot kg^{-1}$],
K_L – a constant related with the energy of sorption [$dm^3 \cdot mg^{-1}$].

The values of q_L and K_L are determined from the slope and intersection of the linear graph of C_{eq}/q_e in the function of C_{eq} [8]. The kinetics of the process of sorption was analysed using a pseudo-secondorder equation:

$$t/q_t = 1/k_2 \cdot q_{cal}^2 + t/q_{cal} \qquad (3)$$

where: q_t – the amount of Triton sorbed during time t [min],
k_2 – the rate constant [$kg \cdot mg^{-1} \cdot min^{-1}$],
q_{cal} – the value of Triton sorption calculated from the equation of kinetics [$mg \cdot kg^{-1}$].

All experiments were made in three replications, and the reported values are arithmetic means of the results. The results concerning the effect of pH, electrolyte and temperature were compared with the results of Triton sorption from water solutions with natural pH and analysed with the method of variance to determine whether there exists a statistically significant difference at $p = 0.05$.

Results

Fig. 1 presents changes in the level of sorption of TX-100 as a function of equivalent concentration.

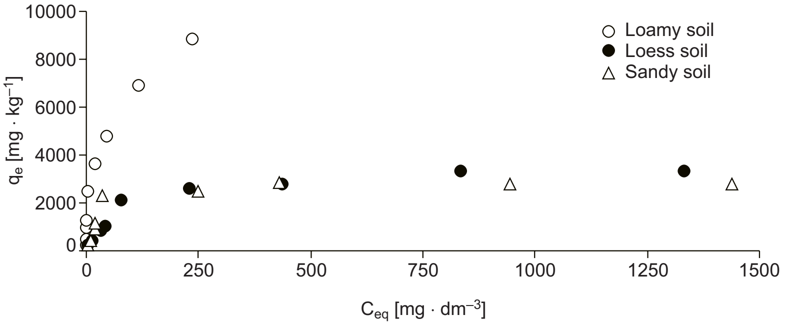

Fig. 1. The sorption of TX-100 in soils

In the loamy soil, sorption of TX-100 increased in a linear manner with increasing concentration of initial solution, but at a degree that decreased as the value of C_{eq} approached the level of 238 mg · dm^{-3}. In the loess and sandy soils, the sorption was initially also linear in character. Above the equivalent concentration, 248 mg · dm^{-3} in the sandy soil and 230.6 mg · dm^{-3} in the loess soil, the sorption increased slightly and attained a constant value in the range of the highest concentrations of C_{eq}. Comparison of the slope of graphs permitted the soils to be arranged in the following series of decreasing sorptive capacity with relation to TX-100: loamy soil > loess soil > sandy soil.

The value of sorption of TX-100 in the soils under study is expressed by percentage sorption that decreased with increase in the initial concentration of the surfactant solution and depended also on the sorptive capacity of the soil. At the maximum initial concentration of 2000 mg · dm^{-3} the percentage sorption of TX-100 was notably lower in the sandy soil (28.7 %) and in the loess soil (33.2 %), compared with the loamy soil (88.3 %) that was characterised by the highest sorptive capacity. At the initial concentration of 50 mg · dm^{-3} the percentage sorption of TX-100 was also the highest in the loamy soil (99.5 %), while in the sandy and loess soils it was at a similar level – at 91.4 % and 91.9 %.

Table 1 gives the parameters for the linear form of Langmuir's isotherm of sorption, and the values of coefficient R^2. High values of the coefficient of correlation R^2 (≥ 0.97) suggest that the Langmuir equation is suitable for the description of TX-100 sorption balance in the soils used in the experiment and within the range of concentrations under study. In the Langmuir equation the value of TX-100 sorption is expressed by the constant q_L. For the sandy, loess and loamy soils the values of constant q_L calculated from the Langmuir equation were comparable to the values of q_e obtained experimentally. Coefficient K_L, that defines the energy of sorption, had the highest value for the sorption of TX-100 in the loamy soil. This may indicate that interactions between TX-100 and the sorptive complex of the loamy soil were stronger than in the case of the loess and sandy soils.

Table 1

Langmuir constants for the sorption of TX-100 in soils

Soil	K_L	q_L	R^2
	$[dm^3 \cdot mg^{-1}]$	$[mg \cdot kg^{-1}]$	
Sandy	0.0269	2932.6	0.99
Loess	0.012	3533.6	0.99
Loamy	0.0696	8849.6	0.97

The graphs given in Fig. 2 present the relation of TX-200 sorption from solutions of various concentrations as a function of duration of contact of the surfactant with the soils. In the graphs, two sections can be distinguished: one, with steeper slope, corresponds to fast sorption, while the other, with notably gentler slope, characterises slow sorption leading to the attainment of the state of saturation. It was found that the rate of sorption was the highest at the beginning of the experiment and decreased gradually with the passage of time. The rate of sorption depended also on the sorptive capacity of the soils and on the concentration of the surfactant. Within the time interval of 5–30 minutes, the rate of sorption (q_t/t) of TX-100 from solution with concentration of 250 mg $\cdot$ dm^{-3} decreased from 44.8 to 25.6 kg $\cdot$ mg^{-1} $\cdot$ min^{-1} in the sandy soil, from 167.1 to 33.5 kg $\cdot$ mg^{-1} $\cdot$ min^{-1} in the loess soil, and from 216.5 to 38.7 kg $\cdot$ mg^{-1} $\cdot$ min^{-1} in the loamy soil. In the case of solution with concentration of 2000 mg dm^{-3} the dynamics of sorption decreased from 85.4 to 34.1 kg $\cdot$ mg^{-1} $\cdot$ min^{-1} in the sandy soil, from 468 to 92.9 kg $\cdot$ mg^{-1} $\cdot$ min^{-1} in the loess soil, and from 1635 to 282.4

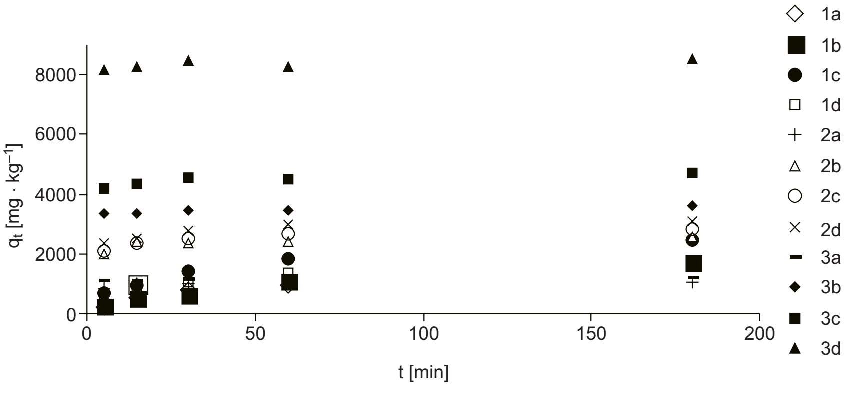

Fig. 2. Kinetics of TX-100 sorption in sandy soil (1), loess soil (2) and loamy soil (3) from solutions with concentrations of: a – 250 mg $\cdot$ dm^{-3}, b – 750 mg $\cdot$ dm^{-3}, c – 1000 mg $\cdot$ dm^{-3}, d – 2000 mg $\cdot$ dm^{-3}; q_t – is the amount of TX-100 sorbed at time t

Table 2

Kinetics parameters for the sorption of TX-100 in soils

C_{in}	Sandy soil				Loess soil				Loamy soil			
$[mg \cdot dm^{-3}]$	q_e	q_{cal}	k_2	R^2	q_e	q_{cal}	k_2	R^2	q_e	q_{cal}	k_2	R^2
	$[mg \cdot kg^{-1}]$		$[kg \cdot mg^{-1} \cdot min^{-1}]$		$[mg \cdot kg^{-1}]$		$[kg \cdot mg^{-1} \cdot min^{-1}]$		$[mg \cdot kg^{-1}]$		$[kg \cdot mg^{-1} \cdot min^{-1}]$	
250	1147.8	1171	$4.3 \cdot 10^{-5}$	0.99	1041.1	1052.6	$5.2 \cdot 10^{-4}$	0.99	1246	1259.4	$8.1 \cdot 10^{-5}$	0.99
750	2502.7	2652.5	$0.3 \cdot 10^{-5}$	0.99	2581.4	2611	$1.1 \cdot 10^{-4}$	0.99	3662.1	3703.7	$3.2 \cdot 10^{-5}$	0.99
1000	2851.9	2857.1	10^{-5}	0.99	2777.8	2824.9	$1.9 \cdot 10^{-4}$	0.99	4782.7	4854.4	$2.7 \cdot 10^{-5}$	0.99
2000	2871.9	2949.8	$0.5 \cdot 10^{-5}$	0.99	3323	3367	$2.4 \cdot 10^{-4}$	0.99	8833.6	8928.6	$1.3 \cdot 10^{-5}$	0.99

kg · mg^{-1} · min^{-1} in the loamy soil. After the 30th minute, until the end of the experiment changes in the rate of TX-100 sorption were notably smaller. This was observable, among other things, in the slight slope of the graphs in the section for the time interval of 30–2280 minutes, and in the low, compared with the 30th minute, rate of sorption in the 48th hour, that amounted to 0.4 kg · mg^{-1} · min^{-1} (sandy soil), 0.36 kg · mg^{-1} · min^{-1} (loess soil) and 0.44 kg · mg^{-1} · min^{-1} (loamy soil) for TX-100 solution with concentration of 250 mg · dm^{-3}, and 0.99 kg · mg^{-1} · min^{-1} (sandy soil), 1.17 kg · mg^{-1} · min^{-1} (loamy soil) and 3.1 kg · mg^{-1} · min^{-1} (loamy soil) for TX-100 solution with concentration of 2000 mg · dm^{-3}. Also the efficiency of sorption displayed a relation to the duration of Triton-soil contact. For example, in the 5th minute the level of sorption of TX-100 from solution with concentration of 250 mg · dm^{-3} was 234 mg · kg^{-1} (sandy soil), 835.5 mg · kg^{-1} (loess soil) and 1082.6 mg · kg^{-1} (loamy soil). With relation to the amount of TX-100 absorbed after 24 hours, those values constituted 20 %, 80 % and 86 %, respectively. In the 30th minute the sorption was at the level of 767.4 mg · kg^{-1} (sandy soil), 1005 mg · kg^{-1} (loess soil) and 1162.5 mg · kg^{-1} (loamy soil), and in comparison with the sorption in the 5th minute it increased by 227.9 % in the sandy soil, 20.4 % in the loess soil, and by 7.4 % in the loamy soil. After 60 minutes the sorption attained the level of 1055.4 mg kg^{-1} in the sandy soil, 1053 mg · kg^{-1} in the loess soil, and 1196 mg · kg^{-1} in the loamy soil, and was 37.5 %, 4.75 % and 2.5 % higher, respectively, with relation to sorption after the 30th minute.

Table 2 gives the parameters of the pseudo-quadratic equation of kinetics. Values of q_{cal} calculated from the equation of kinetics were higher than values of q_e obtained from the experiments, with maximum difference between the values not exceeding 6 %.

Fig. 3 presents sorption of TX-100 from solutions with pH from 1 to 12. In the soils under study, at Triton concentration of 250 mg · dm^{-3}, within the range of pH values from 1 to 12 no statistically significant differences were observed compared with sorption from a solution with natural pH. Also for the concentrations of 750, 1000 and 2000 mg · dm^{-3} at pH from 5 to 10 the changes were practically equal to zero. In all the soils, sorption of TX-100 from solutions with concentrations of 1000 and 2000 mg · dm^{-3} was significantly greater under strongly acidic conditions (pH = 1), and in the

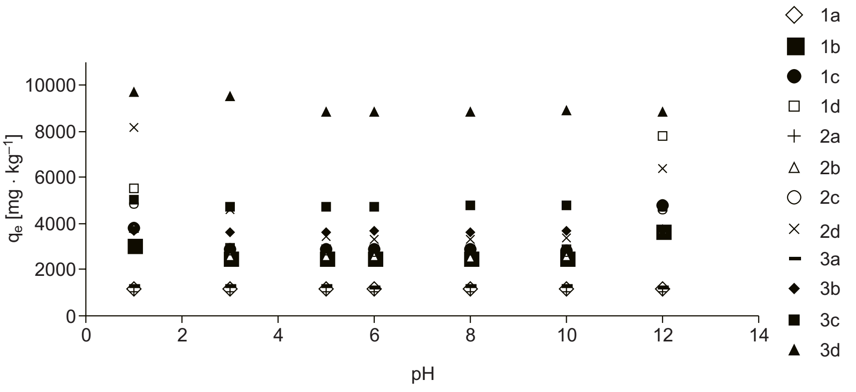

Fig. 3. Effect of pH on the sorption of TX-100 in soils (explanations see Fig. 2)

case of the loess and sandy soil also under strongly alkaline conditions (pH = 12). Moreover, in the loess and loamy soils, at pH = 3 there appeared a significant increase of sorption from the solution with concentration of 2000 mg · dm^{-3}.

The effect of electrolyte was ambiguous: both an increase and a lack of change in the level of Triton sorption were observed (Fig. 4–6) with relation to sorption from solutions without any admixture of KCl, NH_4Cl and $CaCl_2$.

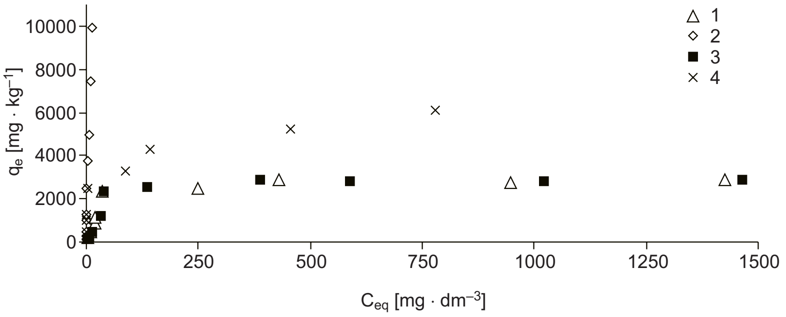

Fig. 4. The sorption of TX-100 in sandy soil: in the absence of electrolyte (1), in the presence of electrolyte: 2 – KCl, 3 – NH_4Cl, 4 – $CaCl_2$

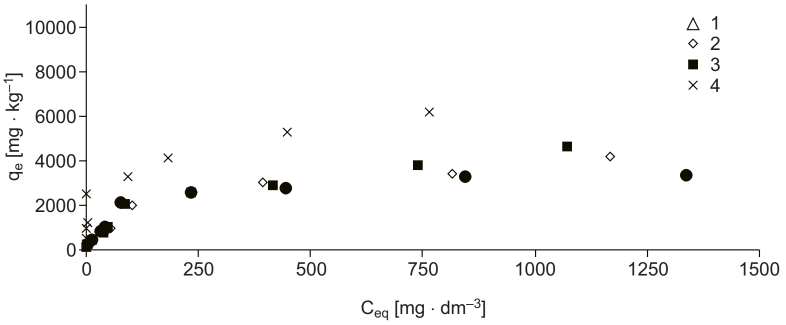

Fig. 5. The sorption of TX-100 in oess soil: in the absence of electrolyte (1), in the presence of electrolyte: 2 – KCl, 3 – NH_4Cl, 4 – $CaCl_2$

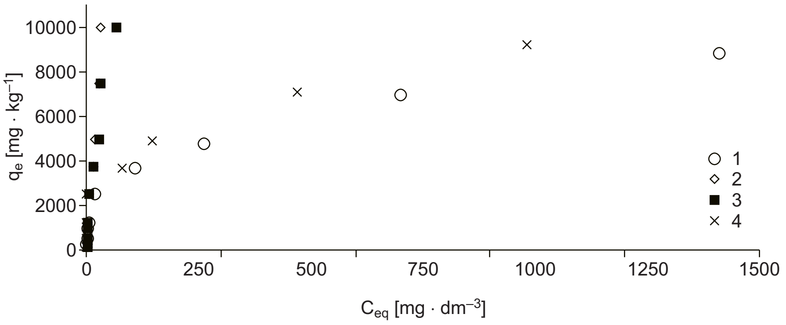

Fig. 6. The sorption of TX-100 in loamy soil: in the absence of electrolyte (1), in the presence of electrolyte: 2 – KCl, 3 – NH_4Cl, 4 – $CaCl_2$

In the loamy soil, a significant increase was observed in Triton sorption from solutions with the highest initial concentrations, ie 1500 and 2000 mg · dm^{-3}. For the solution with the concentration of 1500 mg · dm^{-3}, the sorption increased by 8 % in the presence of KCl and NH_4Cl, and by 2.7 % in the presence of $CaCl_2$.

For the solution with concentration of 2000 mg · dm^{-3}, on the other hand, the increase in sorption was ca 13 % in the presence of KCl and NH_4Cl, and 4 % in that of $CaCl_2$. In the loess soil the presence of KCl and $CaCl_2$ caused a significant increase of sorption within nearly the whole range of initial concentrations, the greatest changes being observed for the solutions with concentrations of 1500 and 2000 mg · dm^{-3}. In the presence of NH_4Cl there was a notable increase of sorption from solutions with concentrations of 1500 and 2000 mg · dm^{-3}, while at lower concentration no significant changes were found. The effect of electrolytes on Triton sorption from solutions with concentrations of 1500 and 2000 mg · dm^{-3} decreased in the sequence of $CaCl_2 > NH_4Cl > KCl$. In the sandy soil, NH_4Cl had no effect on the sorption of Triton. In the same soil, in the presence of KCl and $CaCl_2$, as in the loess soil, a significant increase was noted in triton sorption from all initial solutions. Compared with Triton sorption from solutions without any content of KCl and $CaCl_2$, the greatest differences were observed at concentrations of 1500 and 2000 mg · dm^{-3}. The increase in Triton sorption from solutions of those electrolytes was not uniform. In the presence of KCl, sorption of TX-100 from solution with concentration of 1500 mg · dm^{-3} was 1.4-fold higher, and from solution with concentration of 2000 mg · dm^{-3} – 1.6-fold higher than from solutions with an addition of $CaCl_2$.

Fig. 7 presents the effect of temperature on Triton sorption from solutions with various concentrations. In the sandy and loamy soils, Triton sorption at temperatures > 20 °C was at the same level as at 20 °C or displayed a slight increase of 3–4 %. In the loess soil a few more notable changes were recorded, related with Triton sorption increases within the range of from 8 to 39 %.

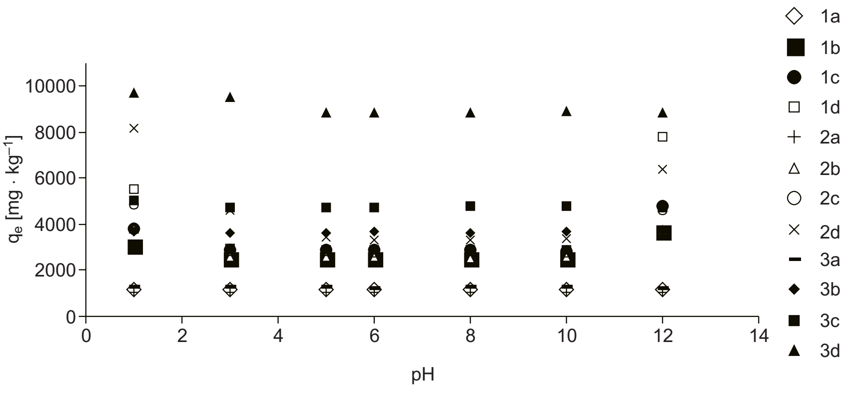

Fig. 7. Effect of temperature on the sorption of TX-100 in sandy soil (1), loess soil (2) and loamy soil (3) from solutions with concentrations of: a – 250 mg · dm^{-3}, b – 750 mg · dm^{-3}, c – 1000 mg · dm^{-3}, d – 2000 mg · dm^{-3}

Discussion

The study showed that sorption of TX-100 in the soils was the highest from solutions with low concentrations of the surfactant. This could have been caused by the fact that the amount of TX–100 in solutions with the lowest concentrations was insufficient for the saturation of the soils under study. For this reason the number of sorption sites potentially available for the sorption of TX-100 from solutions with low concentrations was greater than during sorption from solutions with higher concentrations.

The shape of curves representing the relation of q_e to C_{eq} indicates that the degree of TX-100 sorption in the sandy and loess soils decreased notably when the equivalent concentration of Triton in the solution was close to the value of 1.5 CMC, ie ca 250 $mg \cdot dm^{-3}$. Similar behaviour of surfactants in soils was also observed in other studies [9] and attributed to aggregation of molecules of those compounds [10]. In the loamy soil the equivalent concentration did not exceed the value of 1.5 CMC, and therefore the shape of the sorption curve for that soil was different from those for the sandy and loess soils.

Greater sorption of TX-100 (expressed in %) in the loamy soil with relation to the sandy and loess soils indicates notable differentiation in the sorptive capacity between those soils, resulting from the different physicochemical properties of the soils. The loamy soil showed the greatest affinity to Triton and was characterised by the highest content of clay fractions. The loess soil had the highest content of organic carbon, but a lower share of clay fractions relative to the loamy soil. In the loess soil the sorption of triton oscillated around the same level as in the sandy soil that had the lowest content of organic carbon and of clay fractions. This suggests the supposition that Triton sorption in the soils under study depended to a greater degree on the content of clay fractions than on that of organic carbon.

As follows from the study, sorption of TX-100 from solutions with concentrations of 1500 and 2000 $mg \cdot dm^{-3}$ was significantly higher at pH = 1 and 12 with relation to sorption from solutions with natural pH. Dependence of TX-100 sorption on pH was demonstrated also by Khan and Zareen [8]. According to Paria et al [11], this may indicate participation of hydrogen bonds in the binding of a non-ionic surfactant. In the case of Triton, hydrogen bonds may be formed between oxygen atoms of oxyethylene groups -OCH_2CH_2- of the surfactant and -OH groups on the surface of oxides and on the edges of clay minerals. In an acid environment, -OH groups are non-dissociated and thus capable of forming hydrogen bonds with strongly electronegative atoms of oxygen. In this study, bonding of Triton molecules by soil colloids by means of hydrogen bonds could have been the cause of increased sorption of TX-100 from solutions with low pH. The cause of greater sorption of Triton from a solution with pH = 12 is not known. As it is known, under strongly alkaline conditions there takes place dissociation of -OH groups, and formation of negative charge and dissolution of organic matter. Studies conducted with the use of various surfactants showed both a positive correlation between the level of sorption of those compounds and the content of organic matter [12], and a lack of any distinct effect of that soil component on their sorption [13, 14]. Increase in Triton sorption under conditions in which organic matter was dissolved may suggest that that soil component had only a slight effect on TX-100 sorption in the soils under study.

The effect of KCl, NH_4Cl and $CaCl_2$ on Triton sorption depended on the sorptive capacity of the soil and on the electrolyte cation, and was especially notable in the case of sorption from solutions with the highest concentrations. In principle, the presence of electrolyte caused an increase in Triton sorption, but in certain cases the increase was slight and statistically insignificant. In the loamy soil, electrolytes had a less pronounced effect on Triton sorption. It appears that this resulted from two reasons: firstly, the sorption of TX-100 from solutions without any addition of electrolytes was the highest in the loamy soil, and secondly, K^+, NH_4^+ or Ca^{2+} cations could have been subject to sorption themselves, and to a degree much higher in the loamy soil than in the other soils. This could have been due to the specific physicochemical properties of the loamy soil, and especially to its large specific surface area and the related capacity of the sorptive complex. In the opinion of Zhao and Brown [15], the presence of electrolytes causes removal of water film encasing molecules of a non-ionic surfactant. At the same time there is a reduction in the ease with which hydrocarbon chains dissolve, which may lead – at suitable concentration of the surfactant – to aggregation of its molecules and, consequently, to decrease in the sorption. As in this study an increase was generally observed in the sorption of TX-100 from solutions containing KCl, NH_4Cl and $CaCl_2$, it should be assumed that in the presence of those electrolytes formation of aggregated forms of Triton did not take place.

In the study presented herein, only a slight effect of temperature on the sorption of TX-100 was observed. Kronberg and Silveston [16] are of the opinion that increase in temperature causes a reduction in the degree of hydration of the hydrophilic part of surfactant molecules, which facilitates the formation of aggregates. On the other hand, increase in temperature entails disturbance in the ordered structures of water surrounding the hydrophobic part of surfactants, and that in turn inhibits the formation of aggregates. The relative value of those opposing effects, that display a dependence on the degree of covering of the sorption sites of the sorbent, determines whether surfactant aggregation will take place or not.

Conclusions

1. The level of Triton sorption depended on the capacity of the sorption complex of soil and decreased in the sequence: loamy soil > loess soil > sandy soil.
2. The process of Triton sorption was fast during the initial 30 minutes, following which its dynamics decreased notably.
3. Generally, KCl, NH_4Cl and $CaCl_2$ caused an increase in Triton sorption. The effect of the electrolytes depended on the type of the electrolyte cation, sorptive capacity of the soil, and concentration of the surfactant.
4. Sorption of Triton from solutions with low initial concentrations did not display any relation with the value of pH. The highest increase in Triton sorption was recorded for pH = 1 and 12, for solutions with concentration of 1000 and 2000 $mg \cdot dm^{-3}$.
5. Temperature had only a slight effect on the sorption of Triton in the soils.

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SORPCJA TRITONU X-100 W GLEBACH O RÓŻNYM UZIARNIENIU: KINETYKA, WPŁYW pH, ELEKTROLITU I TEMPERATURY

Katedra Chemii
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Przeprowadzono badania sorpcji surfaktantu tritonu X-100 metodą statyczną przez wytrząsanie 2 g gleby płowej z piasku słabogliniastego, płowej z lessu, brunatnej z gliny ciężkiej w 10 cm^3 roztworu w ciągu 24 godz. Badano także kinetykę procesu i efektywność sorpcji tritonu X-100 z roztworów o różnej wartości (1–12) pH, w obecności elektrolitów: KCl, NH_4Cl i $CaCl_2$ w temperaturach: 20, 25, 30 35 i 50 ^oC. Wyniki doświadczalne wykazywały dobrą zgodność z wynikami obliczonymi z równania Langmuira i równania kinetyki pseudodrugiego rzędu. W glebie gliniastej sorpcja TX-100 wzrastała prawie liniowo w całym przedziale badanych stężeń, natomiast w glebie lessowej i piaszczystej wykazywała liniowy przebieg w zakresie małych stężeń wyjściowych. Stwierdzono dużą szybkość sorpcji w pierwszych 30 min kontaktu TX-100 z glebami, po tym okresie sorpcja zwiększała się wolniej i w mniejszym stopniu. Wartość pH nie miała wpływu na sorpcję surfaktantu z roztworu o stężeniu 250 mg · dm^{-3}. Przy stężeniach 1000 i 2000 mg · dm^{-3} obserwowano znacznie większą sorpcję z roztworów o pH = 1 we wszystkich badanych glebach, a z roztworu o pH = 12 w glebie lessowej i piaszczystej. Obecność elektrolitu powodowała wzrost sorpcji tritonu, ale w stopniu zależnym od rodzaju elektrolitu i właściwości gleby oraz stężenia surfaktanu. Stwierdzono niewielki wpływ temperatury na sorpcję TX-100 w glebach.

Słowa kluczowe: triton X-100, sorpcja, kinetyka, gleba

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Andrzej PLAK[1]

ACCUMULATION AND MIGRATION OF SELECTED FORMS OF ARSENIC AND PHOSPHORUS IN VARIOUSLY UTILIZED LESSIVE SOILS OF LUBLIN

AKUMULACJA I MIGRACJA WYBRANYCH FORM ARSENU I FOSFORU W GLEBACH PŁOWYCH RÓŻNIE UŻYTKOWANYCH MIASTA LUBLINA

Abstract: The results of total arsenic and phosphorus contents as well as selected forms of these elements, in lessive (gray-brown podsolic) soils derived from loess, located in forests and in arable fields in the area of the city of Lublin were presented. An attempt was also made to assess land-use form influence on both elements behaviour. The sequential analysis used for arsenic and phosphorus is based on the scheme proposed by Chang and Jackson, which takes into account the anionic character of arsenic and phosphorus compounds present in soil.

Lessive soils contained from 1.87 up to 12.24 mg · kg^{-1} of arsenic and from 0.16 up to 0.99 g · kg^{-1} of phosphorus. The influence of land use method was observed. Arsenic and phosphorus contents were higher in surface as well as in illuvial horizons of soils located in arable field as compared with forest ones. Fractions of arsenic and phosphorus obtained during analysis showed strong differentiation. Amorphic and crystalline fractions of arsenic bound with iron oxides have the highest share in total arsenic pool. The same situation was noted in the case of phosphorus.

Keywords: arsenic, phosphorus, lessive soils, sequential extraction

A significant source of phosphorus and arsenic in soils, especially in their surface horizons, are mineral fertilizers and pesticides. The behaviour of these two elements in soils depends on their chemical form as well as the composition and physical and chemical properties of soils. The distribution of arsenic and phosphorus, elements that display chemical similarity in soils is characterized by high variability. The occurrence of competition between ions of phosphorus and arsenic sorption on various soil components was described in the literature [1–3]. It mostly results from different sizes

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[1] Department of Soil Science, University of Maria Curie-Skłodowska in Lublin, ul. Akademicka 19, 20–033 Lublin, Poland, phone 81 537 5935, email: aplak@biotop.umcs.lublin.pl

of both anions as well as the different density of the electrical charge distribution. Both ions are subject to sorption by iron and aluminium hydroxides, as well as organic matter [4, 5]. Arsenic and phosphorus are bound by many soil components, so, profile distribution of both elements showed characteristic maximums in surface horizons abundant in humus, as well as in illuvial horizons rich in iron compounds colloidal clay fractions. Phosphorus present in soils in different shapes may successively compete with arsenic ions AsO_4^{3-} in sorption at various soil components. This especially occurs in farming soils fertilized among others with phosphorus compounds, where arsenic specifically fixed to iron and aluminium oxides may be dislodge in certain conditions. The consequence of such procedures is an increase in dissolvable and easily available forms of arsenic in the soil [6]. The effective analysis of both elements is conducted through sequential extraction during which arsenic and phosphorus fractions bound with various soil components are removed. The total content of arsenic and phosphorus in investigated soils does not fully reflect the content form of these elements, but is a very significant environment quality evaluation indicator. The applied sequential extraction of both arsenic and phosphorus is based on an analytical model suggested by Chang and Jackson [7] and differentiating the anion characteristics of arsenic and phosphorus compounds present in the soil [8, 9].

The aim of the study was the determination of total arsenic and phosphorus contents and selected forms of these elements in lessive (grey-brown podsolic) soils derived from loess, gathered in forests and arable fields in Lublin. The evaluation of the influence of soils utilization on the behaviour of both elements was additionally made.

Material and methods

The material under examination represents lessive soils, typical, formed from loess, collected from arable fields and forests. The soil pits were located within Lublin and outside of the Lublin agglomeration influence, in Czeslawice near Naleczow. The following parameters were determined: granulometric composition with the Bouyoucos method modified by Casagrande and Proszynski, sand fraction were separated on sieve with mesh of ∅ 0.1 mm, pH in water and 1 mol $KCl \cdot dm^{-3}$ potentiometrically, organic carbon (organic C) with the Tiurin method, exchangeable cations in 1 mol $NH_4Cl \cdot dm^{-3}$, and cation exchange capacity (T) [10, 11].

The collected samples were sequentially analysed for arsenic according to the Wenzel method [8], and for phosphorus according to Chang-Jackson, modified by Hieltjes-Lijklema [12] (Table 1).

The residue was mineralized by *aqua regia*. The determination of arsenic in all sequential extracts was conducted through generation of hydrides on the AAS 3300 Perkin Elmer spectrometer with the FIAS 400 support, while that of phosphorus with the ascorbic acid method, spectrophotometrically on the Perkin Elmer Lambda 12 spectrophotometer.

Table 1

Sequential analysis model of arsenic and phosphorus extraction in investigated soils

Arsenic fraction	Arsenic extraction conditions	Phosphorus fractions	Phosphorus extraction conditions
As-*sol.* – arsenic forms not specifically fixed with soil components	0.05 mol · dm^{-3} $(NH_4)_2SO_4$, shaking 4 hours, centrifuging, decantation	P-*sol.* – phosphorus forms not specifically fixed with soil components	1 mol NH_4Cl · dm^{-3}, shaking 2 hours (twice), centrifuging, decantation
As-*ex.* – arsenic forms specifically fixed with soil components	0.05 mol · dm^{-3} $(NH_4)H_2PO_4$, shaking 16 hours, centrifuging, decantation	P-*nap.* – phosphorus forms fixed with oxides and hydroxides of iron, aluminium and manganese (non-organic “non-apatite” phosphorus)	0.1 mol · dm^{-3} NaOH, shaking 17 hours, centrifuging, decantation
As-*am.* – arsenic forms fixed with amorphic, hydrated oxides	0.2 mol · dm^{-3} oxalate buffer, pH = 3.25; shaking 4 hours in dark, centrifuging, decantation, cleaning with oxalate buffer through shaking in dark through 10 min	P-*ap.* – phosphorus forms fixed with calcium (non-organic “apatite” phosphorus)	0.5 mol HCl · dm^{-3}, shaking 24 hours, centrifuging, decantation
As-c*r.* – arsenic forms fixed with crystalline oxides	0.2 mol · dm^{-3} oxalate buffer + 0.1 mol · dm^{-3} ascorbic acid, pH = 3.25; in temp. 96 °C, centrifuging, decantation, cleaning with oxalate buffer through shaking in dark through 10 min	P-*org.* – phosphorus forms fixed with organic matter	P-*org* = P-*tot.* – (P-*sol.* + P-*nap.* + + P-*ap.*)
		P-*tot.* – total phosphorus content	*Aqua regia* (16 hours in room temperature + 2 hours in temp. 130 °C
As-*res.* – arsenic residue	*Aqua regia* (16 hours in room temperature + 2 hours in temp. 130 °C, under manoeuvrable radiator)		

Results and discussion

The profiles of investigated lessive soils, which parent material is loess, are created by silty formations. Clearly distinguished is the lessivage process, which resulted in the Bt illuvial horizon development (Table 2).

The pH is mostly strongly acid and acid, while in horizons of the parent material, where there are present carbonates, the pH is above 7.25. Highest content of organic carbon of lessive soils collected in forests and fields was observed in surface horizons, and these values usually decrease with depth. Investigated lessive soils contained from 1.87 to 12.24 mg $\cdot$ kg^{-1} of arsenic and its content did not exceed the limit defined in the Decree of the Polish Minister of Environment on soil and ground quality standards. Arsenic content ranges in forest soils as well as in soils located on arable fields within Lublin boundaries, stay on similar level, when compared with samples taken in Czeslawice near Naleczow. Anthropogenic factors, such as location between dense buildings, roads vicinity, car pollution and recreational utilisation of this area have not decisive influence on arsenic content in soil samples taken in Lublin. The accumulation of this element has primarily been confirmed in illuvial horizons (Bt). The phosphorus content in investigated soils was between 0.16 and 0.99 g $\cdot$ kg^{-1}, with characteristic increase in surface (A) and illuvial horizons (Bt). Therefore the profile distribution of total content of both elements shows much similarity. At the same time it is possible to declare that the strongest influence on phosphorus and arsenic accumulation by the content of organic matter and soil mineral colloids is characteristic for lessive soils. Both elements show strong relationship with the fine soil fractions, which high concentration was observed in Bt horizons. The amounts of phosphates absorbed in soils are higher than those of arsenates. The phosphates are fixed mainly by soil colloids and hydrated oxides of aluminium and iron, while arsenates mainly by oxides and hydroxides of iron [13].

The influence of soil utilization on the profile distribution of arsenic and phosphorus was also observed. Concentration of both elements was higher in surface and illuvial soil horizons located in fields as compared with samples collected in forests.

The fractions of arsenic and phosphorus separated during the sequential extraction showed high diversity (Fig. 1).

The largest share of arsenic in the overall pool belonged to fractions fixed with amorphic and crystalline iron oxides and was as high as over 70 %. The share of analogous fraction of phosphorus counted up to 50 %. For the total pool of arsenic and phosphorus fractions extracted from investigated soils, the amount of mobile fractions and simultaneously available to plants does not exceed 10 %. The share of dissolvable phosphorus fractions, in both forest and farming soils decreases with depth with simultaneous increase of mobile arsenic form (As-*sol* + As-*ex*). There is higher concentration of mobile arsenic forms (As-*sol* + As-*ex*) in lessive soils, and smaller of phosphorus forms in relation to forest soils, which may indicate of sorptive competition of both elements in soil components. The consequence of high affinity of phosphates to soil colloids and hydrated iron and aluminium oxides may be the increase in available arsenic content in the case of soils rich in phosphorus [6].

Table 2

Selected characteristics of lessive soils of Lublin

Profile No.	Location/ Utilisation	Horizon	Depth	$CaCO_3$	pH		Organic C	T	Share of fraction [∅ mm]			
			[cm]	[%]	H_2O	1 M KCl	$[g \cdot kg^{-1}]$	$[mmol(+) \cdot kg^{-1}]$	1–0.1	0.1–0.02	< 0.02	< 0.002
									[%]			
1.	Lublin, Stary Gaj Reserve (forest)	O	3–0	—	5.52	4.92	245.5*	371.9	—	—	—	—
		A	0–23	—	4.69	3.73	8.8	74.0	0.4	59.6	40	9
		Eet	23–48	—	4.52	3.82	4.0	50.2	0.5	58.5	41	7
		EetBt	48–62	—	5.05	3.87	1.1	55.7	0.6	56.4	43	11
		Bt	62–93	—	5.26	3.87	0.9	110.2	0.3	55.7	44	21
		BtC	93–160	—	5.22	3.97	0.6	100.3	0.5	61.5	38	15
		C	> 160	—	5.18	3.96	0.5	85.9	0.6	63.4	36	13
2.	Lublin, Stary Gaj (arable field)	Ap	0–33	—	5.24	3.88	7.7	100.6	0.8	58.2	41	11
		Bt	33–66	—	5.44	3.95	1.6	120.8	0.4	51.6	48	25
		BtC	66–82	—	5.64	4.05	0.8	69.0	0.8	65.2	34	13
		C	82–146	—	5.72	4.09	0.6	81.1	0.5	61.5	38	15
		Cca	< 146	4.32	8.15	7.25	0.7	496.8	0.6	63.4	36	13

Table 2 contd.

Profile No.	Location/ Utilisation	Horizon	Depth	$CaCO_3$	pH		Organic C	T	Share of fraction [∅ mm]			
			[cm]	[%]	H_2O	1 M KCl	[g · kg^{-1}]	[mmol(+) · kg^{-1}]	1–0.1	0.1–0.02	< 0.02	< 0.002
									[%]			
3.	Czeslawice near Naleczow (forest)	O	1–0	—	5.55	4.98	694.1*	745.5	—	—	—	—
		A	0–7	—	4.17	3.41	32.5	165.8	0.4	60.6	39	13
		AEet	7–16	—	4.95	3.75	7.9	382.2	0.4	59.6	40	12
		Bt	16–50	—	5.31	3.66	1.8	98.7	0.3	52.7	47	25
		BtC	50–70	—	5.63	3.83	1.4	75.4	0.3	59.7	40	20
		C	70–129	—	6.05	4.12	0.8	60.8	0.3	68.7	31	14
		Cca	< 129	10.04	8.69	7.85	0.6	628.2	0.6	61.4	38	14
4.	Czeslawice near Naleczow (field)	ApBt	0–15	—	5.23	4.66	7.8	112.5	0.2	57.8	42	13
		B1t	15–40	—	5.18	4.59	1.3	92.2	0.2	45.8	54	27
		B2t	40–65	—	5.11	4.43	0.8	82.0	0.1	42.9	57	31
		B2tC	65–90	—	5.09	4.42	0.4	69.3	0.1	43.9	56	26
		C	90–150	—	4.20	4.53	0.4	87.0	0.2	48.8	51	21
		Cca	< 150	7.97	8.32	7.64	0.2	509.8	0.1	59.9	40	14

* Organic matter.

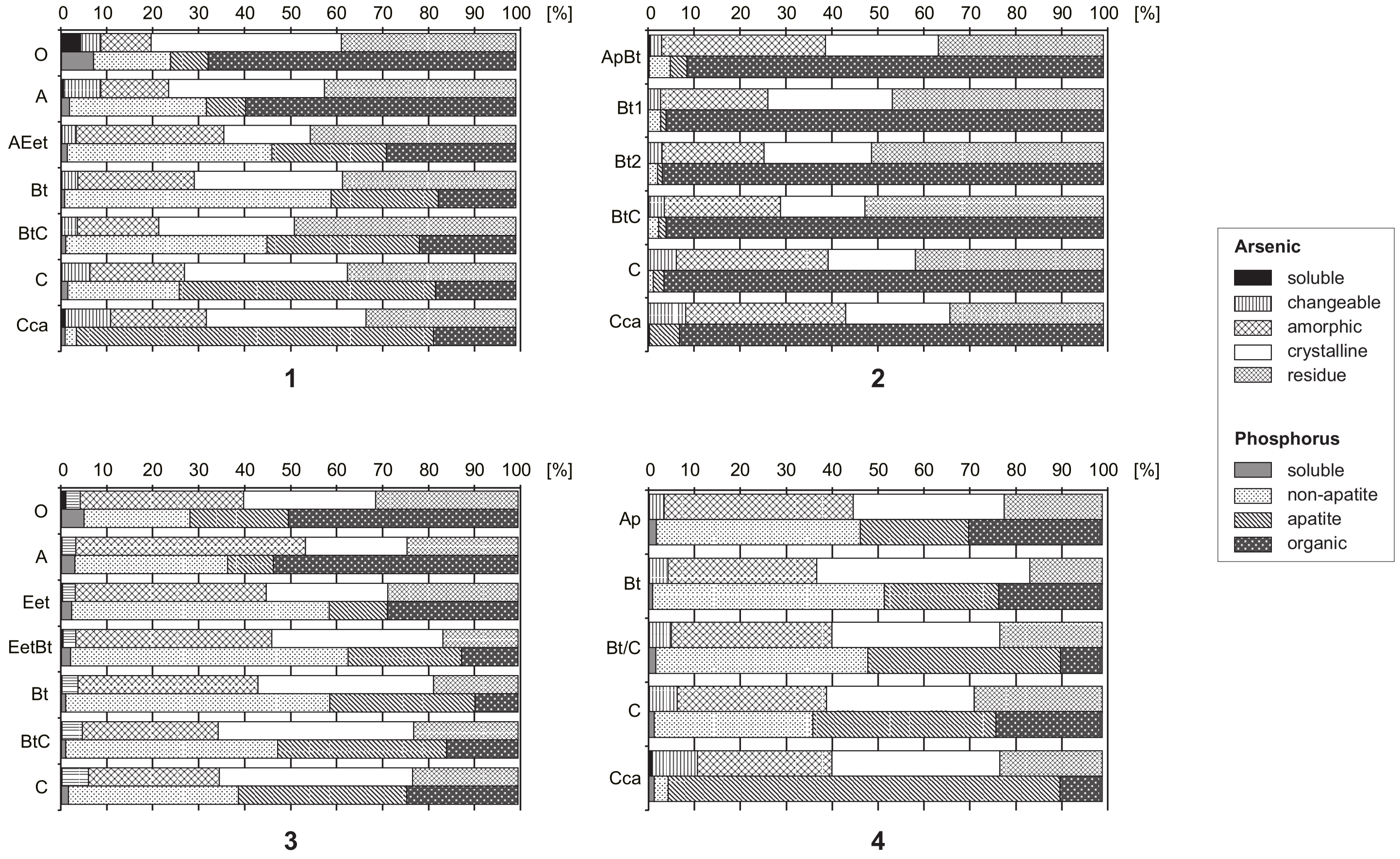

Fig. 1. Share [%] of determined As and P fractions in lessive soils of different utilization. 1 and 2: profiles beyond agglomeration influence (1 – forest, 2 – field); 3 and 4: profiles located within the city boundaries (3 – forest, 4 – field)

A regularity is also recognized that the higher phosphorus content in A horizons of lessive soils collected from fields was connected with the higher share of mobile arsenic forms. Fixation of arsenic and phosphorus by many soil components causes their gathering in surface horizons. It was especially observed in places subject to strong anthropopression (eg cities) what is connected with accumulation of various pollutants as well as fertilization. However the comparison of both elements content in soils located within Lublin as well as in Czeslawice near Naleczow shows small influence of the Lublin agglomeration. The profile distribution of arsenic and phosphorus content has a similar pattern.

Conclusions

1. The influence of land utilization on the content of arsenic and phosphorus is observed. The content of both elements was higher in soils located in fields than in forests ones.
2. The influence of the Lublin agglomeration on the content of both elements is slight. The contents of arsenic and phosphorus are at similar levels in lessive soils collected both in Lublin and outside of the Lublin agglomeration.
3. The highest share in the total pool of arsenic and phosphorus is held by fractions of limited mobility (associated with iron, aluminium, manganese oxides or calcium compounds).
4. Lessive soils utilized agriculturally have a higher share of mobile arsenic fractions (As-*sol* + As-*ex*), and lower of phosphorus fractions (P-*sol*) as compared with the investigated forest soils.

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AKUMULACJA I MIGRACJA WYBRANYCH FORM ARSENU I FOSFORU W GLEBACH PŁOWYCH RÓŻNIE UŻYTKOWANYCH MIASTA LUBLINA

Zakład Gleboznawstwa
Uniwersytet Marii Curie-Skłodowskiej w Lublinie

Abstrakt: Przedstawiono wyniki oznaczeń całkowitych zawartości arsenu i fosforu oraz wybranych frakcji tych pierwiastków w glebach płowych wytworzonych z lessu, pobranych w lesie i na polu uprawnym na terenie miasta Lublina. Podjęto także próbę oceny wpływu użytkowania na zachowanie się obu pierwiastków. Zastosowana sekwencyjna ekstrakcja zarówno arsenu, jak i fosforu korzysta ze schematu analitycznego zaproponowanego przez Changa i Jacksona, uwzględniającego anionowy charakter występujących w glebie związków arsenu i fosforu.

Badane gleby płowe typowe zawierały od 1.87 do 12.24 mg arsenu $\cdot$ kg^{-1}, a zawartość fosforu wahała się od 0.16 do 0.99 g $\cdot$ kg^{-1}. Jednocześnie zaznaczył się także wpływ sposobu użytkowania gleb. Zawartości arsenu i fosforu były większe w poziomach powierzchniowych. Obserwowano też wzbogacenie w te pierwiastki gleb z pola uprawnego w stosunku do próbek glebowych pobranych w lesie. Zawartość frakcji arsenu i fosforu wydzielonych w analizie specjacyjnej wykazywała duże zróżnicowanie. Największy udział arsenu w ogólnej puli tego składnika miały frakcje związane z amorficznymi i krystalicznymi tlenkami żelaza. Analogiczne zależności stwierdzono też w przypadku fosforu.

Słowa kluczowe: arsen, fosfor, gleby płowe, sekwencyjna ekstrakcja

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Barbara SKWARYŁO-BEDNARZ[1] and Anna KRZEPIŁKO[1]

EFFECT OF VARIOUS DOSES OF NPK FERTILIZERS ON CHLOROPHYLL CONTENT IN THE LEAVES OF TWO VARIETIES OF AMARANTH (*Amaranthus cruentus* L.)

WPŁYW ZRÓŻNICOWANYCH DAWEK NAWOZÓW NPK NA ZAWARTOŚĆ CHLOROFILU W LIŚCIACH DWÓCH ODMIAN AMARANTUSA (*Amaranthus cruentus* L.)

Abstract: The effect of various doses of NPK fertilizers on chlorophyll content in the leaves of two varieties of amaranth, ‘Rawa’ and Aztek, was investigated. In field experiments amaranth was grown at narrow spacing on good wheat complex soil in South-Eastern Poland. The following combinations of macroelement doses were applied: I – 50 kg N, 40 kg P and 40 kg K · ha^{-1}, II – 70 kg N, 50 kg P and 50 kg K · ha^{-1}, III – 90 kg N, 60 kg P and 60 kg K · ha^{-1} and IV – 130 kg N, 70 kg P and 70 kg K · ha^{-1}. Assessments were made of chlorophyll *a*, *b* and *a*+*b* content in fresh leaf tissue during the full bloom and seed formation stages.

The chlorophyll a content in the ‘Rawa’ amaranth leaves was found to be higher than in the ‘Aztek’ leaves. In both varieties analysed, the values for this parameter were higher during seed formation than in the bloom stage. The highest chlorophyll *a* content in the ‘Rawa’ variety was found with combination III of NPK fertilizer, while for ‘Aztek’ it was highest with combination II. Chlorophyll *b* content was higher per unit fresh mass of ‘Rawa’ leaves than in the ‘Aztek’ variety. The highest chlorophyll *b* content per unit fresh mass of ‘Rawa’ leaves was found with combination II of macroelement fertilizers, while for ‘Aztek’ this value was highest with combination III. Statistically significant dependencies were found between the NPK fertilizer doses used and the amount of chlorophyll in the fresh leaf tissue of both amaranth varieties.

Keywords: chlorophyll, amaranth (*Amaranthus cruentus* L.), NPK fertilization, doses

Chlorophylls take part in biosynthesis processes occurring in the green parts of plants. Together with carotenoids, they participate in the process of light energy absorption and its conversion to chemical energy, which is used in the endoergic process of synthesizing organic compounds from the simple substances: carbon dioxide and H_2O [1]. Numerous studies have shown that chlorophyll content in plants increases sharply following fertilization with macroelements, particularly nitrogen [2]. Amaranth

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[1] Faculty of Agricultural Sciences in Zamosc, University of Life Sciences in Lublin, ul. Szczebrzeska 102, 22–400 Zamość, Poland, phone 84 677 27 56, email: bskwarylo@wnr.edu.pl

is a plant that reacts quickly to nitrogen fertilization, and its varieties used as vegetables or animal fodder react particularly well to this macroelement. Most commonly recommended for amaranth cultivation is nitrogen at 80–120 kg N · ha^{-1} in the form of Polifoska or ammonium nitrate, phosphorus at 50–70 kg P · ha^{-1}, in the form of Polifoska or superphosphates, and potassium at 50–70 kg K · ha^{-1} in the form of Polifoska or potassium chloride [3].

The aim of this study was to assess the effect of various doses of NPK fertilizer on chlorophyll content in the leaves of two varieties of amaranth (*Amaranthus cruentus* L.).

Material and methods

A field experiment was conducted in 2007 on a farmer's field situated near Zamosc. The aim of the experiment was to determine the effect of various doses of NPK on chlorophyll content in two varieties 'Rawa' and 'Aztek' of amaranth (*Amaranthus cruentus* L.) cultivated for seed. The brown soil on which the experiment was conducted was characterized by very high N content and high P, K and Mg content. The experiment was set up in a random split-plot design with three replicates. The following combinations of NPK doses were used: I – 50 kg N, 40 kg P and 40 kg K · ha^{-1}, II – 70 kg N, 50 kg P and 50 kg K · ha^{-1}, III – 90 kg N, 60 kg P and 60 kg K · ha^{-1} and IV – 130 kg N, 70 kg P and 70 kg K · ha^{-1}.

Nitrogen fertilizer in the form of ammonium nitrate was applied twice, before sowing and during the intensive growth period. Phosphorus and potassium fertilisers were applied before sowing – P in the form of Polifoska and K in the form of potassium chloride. The results obtained were compared with the control (with no NPK fertilisation). Amaranth seeds were sown during the last decade of May at narrow spacing (every 30 cm). The area of the experimental microplots from which the plants were to be harvested was 1 m^2. The plants were cultivated in accordance with proper horticulture procedures. The spectrophotometric method described by Blamowski and Borowski [4] was used to determine chlorophyll *a* and *b* content as well as the total (*a*+*b*) chlorophyll content in the leaves. The measurements were made during the flowering stage and again at the onset of seed formation, using the third green leaf of the plant counting downward from the inflorescence. All measurements were made in three replicates.

Results and discussion

Fertilization with the various doses of macroelements contributed to an increase in chlorophyll *a* and *b* and total chlorophyll in the amaranth leaves (Table 1), but a statistically significant correlation was found only for they amount in the flowering stage (Table 2).

The high macroelement doses applied in NPK combination IV resulted in lower chlorophyll content than was noted in the samples where less intense fertilization had been applied. However, even for this combination the chlorophyll content was higher than in the control.

Table 1

Effect of NPK fertilization on chlorophyll content in amaranth leaves

Combination	Average chlorophyll content [mg · g^{-1} fresh mass]							
	Flowering stage				Beginning of seed formation			
	a	*b*	total	*a*:*b* ratio	*a*	*b*	total	*a*:*b* ratio
‘Rawa’ variety								
Control	0.356	0.270	0.626	1.32:1	1.025	0.230	1.255	4.47:1
I	0.361	0.282	0.643	1.28:1	1.034	0.240	1.274	4.31:1
II	0.520	0.377	0.897	1.38:1	1.041	0.253	1.294	4.11:1
III	0.588	0.374	0.962	1.57:1	1.448	0.245	1.693	5.91:1
IV	0.510	0.350	0.860	1.46:1	1.032	0.231	1.263	4.47:1
‘Aztek’ variety								
Control	0.230	0.198	0.428	1.16:1	0.750	0.181	0.931	4.14:1
I	0.237	0.208	0.445	1.14:1	0.774	0.184	0.958	4.21:1
II	0.802	0.360	1.162	2.23:1	1.137	0.221	1.358	5.14:1
III	0.760	0.379	1.139	2.01:1	0.997	0.370	1.367	2.69:1
IV	0.710	0.362	1.072	1.96:1	0.921	0.280	1.201	3.29:1

‘Rawa’ amaranth leaves had higher chlorophyll a content than leaves of ‘Aztek’ variety. In both varieties a statistically significant correlation was found between dose of macroelement fertilizers and chlorophyll *a* content in the leaves at flowering stage (Table 2).

Table 2

Correlation coefficients between macroelement doses and chlorophyll content in the leaves

Parameter	Stage of plant growth	
	flowering stage	beginning of seed formation
‘Rawa’ variety		
Chlorophyll *a* content	0.747**	0.268
Chlorophyll *b* content	0.736**	0.138
Total chlorophyll content	0.705**	0.325
‘Aztek’ variety		
Chlorophyll *a* content	0.763**	0.529
Chlorophyll *b* content	0.823**	0.675*
Total chlorophyll content	0.543	0.657

Significance level: * $\alpha = 0.05$, ** $\alpha = 0.01$.

The highest chlorophyll *a* content in the leaves of the ‘Rawa’ variety was noted with NPK applied in dose of 90 kg N, 60 kg P and 60 kg K · ha^{-1} (combination III) (Table 1).

The macroelements application caused a 39.5 % increase in chlorophyll *a* content in the leaves in the flowering stage, and a 41.3 % increase in the seed formation stage, in comparison with the plants of control combination.

The average chlorophyll *a* content for the 'Aztek' variety was the highest after macroelements application in doses of 70 kg N, 50 kg P and 50 kg K $\cdot$ ha^{-1} (combination II) (Table 1) and was by 248.7 % higher than the control plants in the flowering stage, and by 51.6 % at the beginning of seed formation.

The average chlorophyll *b* content was higher in leaves of the 'Rawa' variety than in the 'Aztek' variety. The level of chlorophyll *b* in 'Rawa' leaves measured in the flowering stage was higher than in the seed formation stage. The greatest increase in chlorophyll *b* in the leaves of this variety was found after application of 70 kg N, 50 kg P and 50 kg K $\cdot$ ha^{-1} (combination II) and was by 39.6 % higher than in the control plants (Table 1). Statistical analysis confirmed that chlorophyll *b* content in 'Rawa' leaves was dependent on the NPK fertilizers applied only in the flowering stage (Table 2).

Chlorophyll *b* content in the leaves of the 'Aztek' variety was higher in the flowering stage than in the seed formation stage. Application of macroelements in doses of 90 kg N, 60 kg P and 60 kg K $\cdot$ ha^{-1} (combination III) caused a 91.4 % increase in chlorophyll *b* in the flowering stage and a 104.4 % increase at the beginning of seed formation stage, in comparison with the plants of control combination. The level of chlorophyll *b* in 'Aztek' leaves was positively correlated with the amount of fertilizer added, irrespective of when the plant material was collected (Table 2).

Total chlorophyll content in the plants was also dependent on the variety of amaranth. The average total chlorophyll content was higher in the seed formation stage than in the flowering stage. The highest total chlorophyll content was noted in 'Rawa' leaves during the seed formation stage after application of NPK fertilizers in dose of 90 kg N, 60 kg P and 60 kg K $\cdot$ ha^{-1} (combination III) and amounted 1.693 mg $\cdot$ g^{-1} fresh mass. In the flowering stage the value of this parameter for the same fertilizer dose was by 75.9 % lower.

In the 'Aztek' variety, NPK fertilizers used in dose of 70 kg N, 50 kg P and 50 kg K $\cdot$ ha^{-1} (combination II) had the most beneficial effect on total chlorophyll level in the flowering stage. In this case the chlorophyll content was by 71.5 % higher than in the control plants (Table 1). Fertilizers application in dose of 90 kg N, 60 kg P and 60 kg K $\cdot$ ha^{-1} (combination III) had the most beneficial effect on total chlorophyll content in leaves at the beginning of seed formation stage and caused its increase by 45.9 % in comparison with the control plants. A statistically significant positive correlation ($r_{0.01} = 0.705$) between the total chlorophyll content in the amaranth leaves and the dose of fertilizers applied was found only for the 'Rawa' variety in the flowering stage (Table 2).

The increase in total chlorophyll content in the leaves was probably generated by the level of NPK fertilization. According to Ciecko et al [2], the greater amount of NPK fertilizers is accompanied by the higher total chlorophyll content in plant material. According to Nalborczyk et al [3], nitrogen fertilization affects chlorophyll content in plants. Research by Peyvast et al [5] shows that the level of chlorophyll in plants increases rapidly following application of organic fertilizer. Coops et al [6] suggest that the level of chlorophyll – *a*, *b* and total – in leaves is dependent not only on the species of plant, but also on the variety. The results of the present study on amaranth confirmed results of other authors [2]. Most varieties of sugar beet, including 'Khazar', react positively to an increase in NPK fertilizer with an increase in chlorophyll *b* in the leaves. Gebczyński [7] suggests that the amount of total chlorophyll in plants can fluctuate. The main factor affecting the changeability of this parameter may be the variety of the plant. It is assumed that chlorophyll *a* and chlorophyll *b* usually occur in plants at a 3:1 ratio [8, 9].

The highest ratio of chlorophyll *a* to *b* was found, both for 'Rawa' and 'Aztek' leaves, at the beginning of seed formation stage after NPK application in dose of 90 kg N, 60 kg P and 60 kg K $\cdot$ ha^{-1} (combination III).

Conclusions

1. The NPK fertilization application cause an increase in chlorophyll content in the amaranth leaves. For the 'Rawa' variety, the highest chlorophyll *a* and total chlorophyll content is noted with NPK application in dose of 90 kg N, 60 kg P and 60 kg K $\cdot$ ha^{-1} (combination III), while the highest chlorophyll *b* content when NPK dose are of 70 kg N, 50 kg P and 50 kg K $\cdot$ ha^{-1} (combination II). For the 'Aztek' variety, the highest chlorophyll *a* content is found with combination II, while the highest chlorophyll *b* and total chlorophyll content with combination III.

2. A statistically significant correlation between the NPK fertilizers doses applied and chlorophyll content in the 'Rawa' and 'Aztek' leaves was found in the flowering stage of the plants.

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WPŁYW ZRÓŻNICOWANYCH DAWEK NAWOZÓW NPK NA ZAWARTOŚĆ CHLOROFILU W LIŚCIACH DWÓCH ODMIAN AMARANTUSA (*Amaranthus cruentus* L.)

Wydział Nauk Rolniczych
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Badano wpływu zróżnicowanego nawożenia NPK na zawartość chlorofilu w liściach dwóch odmian szarłatu ‘Rawa’ i ‘Aztek’. Szarłat uprawiano w doświadczeniu polowym w rozstawie wąskorzędowej na glebie kompleksu pszennego dobrego, w środkowo-wschodniej części Polski. Zastosowano następujące kombinacje dawek makroskładników: I – 50 kg N, 40 kg P i 40 kg K · ha^{-1}, II – 70 kg N, 50 kg P i 50 kg K · ha^{-1}, III – 90 kg N, 60 kg P i 60 kg K · ha^{-1} oraz IV – 130 kg N, 70 kg P i 70 kg K · ha^{-1}. Oznaczono zawartość chlorofilu *a* i *b* oraz sumę chlorofili *a+b* w świeżej masie liści w stadium pełni kwitnienia roślin oraz na początku formowania nasion. Z przeprowadzonych badań wynika, że liście szarłatu odmiany ‘Rawa’ zawierały więcej chlorofilu niż liście odmiany ‘Aztek’. Zawartości chlorofilu w liściach badanych odmian szarłatu były większe w okresie formowania nasion niż w okresie kwitnienia. Liście szarłatu odmiany ‘Rawa’ zawierały najwięcej chlorofilu *a* po zastosowaniu nawożenia NPK w dawce 90 kg N, 60 kg P i 60 kg K · ha^{-1} (kombinacja III), natomiast liście odmiany ‘Aztek’ po zastosowaniu 70 kg N, 50 kg P i 50 kg K · ha^{-1} (kombinacja II). Notowane ilości chlorofilu *b* były większe w świeżej masie liści odmiany ‘Rawa’ w porównaniu z odmianą ‘Aztek’. Największą zawartość chlorofilu *b* stwierdzono w świeżej masie liści odmiany ‘Rawa’ po zastosowaniu II kombinacji nawożenia, a w liściach odmiany ‘Aztek’ po zastosowaniu III kombinacji nawożenia NPK. Stwierdzono statystycznie istotne zależności pomiędzy zastosowanymi dawkami nawozów NPK a zawartością chlorofilu w świeżej masie liści obu odmian szarłatu.

Słowa kluczowe: chlorofil, szarłat (*Amaranthus cruentus* L.), nawożenie NPK, dawki

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Agata ŚWIĘCIŁO[1]

EFFECT OF ENERGY METABOLISM OF THE *Saccharomyces cerevisiae* YEAST CELLS VS MENADIONE TOXICITY

METABOLIZM ENERGETYCZNY KOMÓREK DROŻDŻY *Saccharomyces cerevisiae* A TOKSYCZNOŚĆ MENADIONU

Abstract: Menadione (2-methyl-1,4-naphthoquinone) is a prooxidant agent commonly used in laboratory practice. It can induce oxidative damage to many cell biomolecules. The results of earlier studies show that the efficiency of the antioxidant system plays a significant part in the protection of yeast cells from toxic effects induced by menadione. The purpose of this study was to determine the sensitivity of *Saccharomyces cerevisiae* yeast cells with different types of energy metabolism to menadione. The cells of the wild strain SP4 and its isogenic respiratory mutant SP4rho^{-} were used in the experiment. By growing yeast on media containing different carbon sources (fermentable and non-fermentable) cells of different respiratory activity were obtained. The viability of the yeast cells was determined by calculating the colonies grown on solid media in the presence of this prooxidant.

Under condition of full respiratory activity of yeast in the presence of the non-fermentable carbon source, ie ethanol, greater sensitivity of yeast cells to menadione was observed than under conditions of repression of the respiratory system (medium containing 2 % or 10 % glucose) in the case of cells of mutants incapable of aerobic respiration and in the presence of the slightly fermentable carbon source, ie raffinose.

The results obtained show that the toxicity of menadione is not only connected with the efficiency of cell antioxidant mechanisms but it also depends on the type of energy metabolism of yeast cells.

Keywords: menadione, yeast, energy matabolism

Menadione (2-methyl-1,4-naphthoquinone) is a prooxidating agent, commonly used in laboratory practice, which is known to produce high fluxes of superoxide *in vivo* via a redox-cycling mechanism. Increased production of superoxide anion-radical and hydrogen peroxide, which is a product of a dismutation reaction of superoxide anion-radical disturbs the redox homeostasis in a cell [1]. It can result in oxidating modifications of many cell biomolecules. Studies by Cabiscol et al [2] show that oxidated forms of cytoplasmic and mitochondrial proteins appear both in aerobically

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[1] Chair of Biochemistry and Environmental Chemistry, Faculty of Agricultural Sciences in Zamosc, University of Life Sciences in Lublin, ul. Szczebrzeska 102, 22–400 Zamość, Poland, email: aswiecilo@libero.it

and anaerobically respiring yeast cells in the presence of menadione and hydrogen peroxide. A decrease of the level of their activity was also observed under these conditions. Other very important targets for menadione are the unsaturated fatty acids in cell membranes. In the presence of menadione an increase of the levels of lipid peroxidation expressed as concentration of malondialdehyde (MDA), a final product of lipid oxidation was observed in yeast cells [3].

Yeast cells possess a complex system neutralizing the deleterious effects of menadione. The most critical component of the protective system consists of antioxidant enzymes. The activity of superoxide dismutases located in the cytoplasm and mitochondrial matrix, various peroxidases, particularly catalases, glutathione transferases [4, 5] and of glutathione [6] play an important role in this system.

So far there is little data about the influence of the metabolic status of the cell on the toxicity of this prooxidating compounds.

Depending on environmental conditions (carbon source, oxygen availability) the *S. cerevisiae* yeast cells can obtain the energy necessary for life processes by aerobic respiration or fermentation. When inoculated into a medium rich in glucose (irrespective of oxygen availability) *S. cerevisiae* cells can convert glucose to ethanol by “fermentation”, budding yeast‘s preferred method of metabolism. Pathways for the assimilation of alternative carbon sources are repressed under these conditions. The cells which grow in the presence of glucose are characterized by high activity of glycolysis pathway, decrease in respiratory activity, increase in ribosome biogenesis as well as fast cell divisions and short cell cycles.

Yeast can utilize other energy/carbon sources only after glucose exhaustion. The preferred energy/carbon source after exhausting of glucose is ethanol, which is available in high concentrations at that point. Ethanol just like glycerol and lactate is a non-fermentable carbon source for yeast cells and can be metabolized only in the aerobic respiration process. The shift from fermentation of glucose to aerobic respiration of ethanol is called the “diauxic shift” and is known to be accompanied by major changes in gene expression [7]. A wide variety of enzymes induced during the diauxic shift enable yeast cells to live in ethanol supplemented media. These include enzymes involved in gluconeogenesis, the glyoxylate cycle, the tricarboxylic acid cycle and respiration [8, 9]. In ethanol supplemented media the cells grow slower and have a tendency to invasive and filamentous growth in response to nitrogen starvation [10].

In the media which contain non-fermentable carbon sources (ethanol, glycerol) mitochondrial yeast mutants (*rho*$^-$ and *rho*^{0} mutants) cannot grow. They are characterized by large deletions of mitochondrial genome or its total loss, which results in their deprivation of a functional respiratory chain. They can be easily obtained in laboratory conditions and therefore constitute a convenient object for examining the role of oxygen metabolism in toxicity induced by different substances.

Yeast cells can also use certain oligosaccharides, such as raffinose or maltose. Trisaccharide raffinose (α-galactosyl-α-glucosyl-β-fructose) is hydrolised by the periplasmic invertase to fructose and melibiose [11]. Fructose is then transported into the cells by glucose permeases [12]. It is hypothesised that in many yeast species the permease activities for this particular saccharide are not sufficient to ensure the high substrate flow necessary for fermentative growth. This is why it is mainly utilized in aerobic respiration. The remaining disaccharide (melibiose) is assimilated in *S. cerevisiae* cells by the product of several MEL genes encoding α-galactosidase [13–15]. For this reason why the cells of wild strains grow fast on raffinose and the mutants incapable of aerobic respiration grow very slowly and form small colonies.

The main purpose of the study was to examine the level of sensitivity of the *S. cerevisiae* yeast cells differing in energetic metabolism to menadione. The viability of the wild type of cells and its respiratory mutant was determined in the presence of menadione added in solid media containing 2 % and 10 % glucose, 2 % raffinose and ethanol as the sole sources of carbon.

Material and methods

The characteristics of the *Saccharomyces cerevisiae* yeast strains selected for experiments:

– SP-4 wild strain (*wt*) of genotype: Mat α leu1 arg4 [16],

– SP-4*rho*$^-$ respiratory mutant obtained as a result of threefold passaging of isogenic cells of respiratory competent strain (Sp4*rho*$^+$) in the presence of ethidium bromide [17].

The *rho*$^-$ strain were selected by their inability to grow on plates containing ethanol as the sole carbon source.

Yeast growth conditions

The yeast was grown in liquid medium YPD containing: 10 g · dm^{-3} of yeast extract, 10 g · dm^{-3} of peptones, 20 g · dm^{-3} of glucose. The yeast culture in liquid medium was conducted in aerobic conditions at temp. 28 °C for 48 hours in order to obtain a culture of cells at stationary stage of growth (STAT cells). They were used to inoculate solid media containing different sources of carbon and different concentrations of menadione.

Menadione treatments

To dissolved media containing: 10 g · dm^{-3} of peptone, 10 g · dm^{-3} of yeast extract, 20 g · dm^{-3} of agar and different concentrations of saccharides: 20 g · dm^{-3} of glucose (2 %), 100 g · dm^{-3} of glucose (10 %), 20 g · dm^{-3} raffinose (2 %) or 20 cm^3 · dm^{-3} of ethanol different volumes of menadione solution in concentration of 10 mg·cm^{-3} were added to obtain 0, 5, 7.5, 10, 12.5, 15, 17.5, 20 and 22.5 μg · cm^{-3} concentration of this substance. 0.1 cm^3 of suspension of yeast cells obtained after diluting stationary cells (STAT cells) was sown on the media prepared in the above-described way. They were incubated at temperature 28 °C for 48 hours. The number of colonies forming units (CFU) which grew on the dishes indicated the viability of the cells under these conditions. The number of CFU which grew on the medium without menadione was assumed to be 100 %.

The menadione preparation was purchased at Sigma Chemical C.O., glucose and ethanol at POCH, Poland and the remaining reagents used for preparing the media at Difco. The presented results are a mean from at least four independently conducted experiments.

Results

The viability of yeast cells of the wild strain and of its isogenic mutant Sp4*rho*$^{-}$ was examined in the media containing different respiratory substrates supplemented with menadione (Table 1).

Table 1

Survival rate of yeast cells of the SP4*wt* strain and SP4r*ho*$^{-}$ in solid culture media containing different respiratory substrates and menadione

Menadione concentration [μg · cm^{-3}]	Culture conditions/yeast strains				
	Glucose			Ethanol	Raffinose
	2 %/mass	10 %/mass	2 %/*rho*$^{-}$	2 %/mass	
0	100.0	100.0	100	100	100
5	105.2	103.4	90.4	80.6	93.6
7.5	105.6	97.5	84.8	0	84.1
10	98.1	99.4	80.5	0	80.5
12.5	82.4	63.3	84.9	0	84.8
15	74.3	35.2	70.6	0	90.4
17.5	2.1	5.2	65.3	0	91.3
20	0	0	77.3	0	37.8
22	0	0	20.1	0	0

The conditions of the experiment produce the effects of long-term action of menadione on yeast cells. They are also continuously exposed to the toxic substance. The yeast cells of the wild strain grown in the presence of low (2 %) and high (10 %) concentrations of glucose in the culture media are characterized by a higher resistance to menadione than the cells of the same strain grown in the presence of non-fermentable carbon source, ie ethanol. In this case, after application of menadione in concentration exceeding 5 μg · cm^{-3} no growth of these cells was observed. The cells grown on fermentable carbon source (glucose) were characterized by a decreased viability after application of menadione in concentration exceeding 12.5 μg · cm^{-3}. Total loss of colony-forming ability was observed in this case at menadione concentration exceeding 17.5 μg · cm^{-3}. The cells of respiratory deficient mutant (*rho*$^{-}$) grown on glucose behaved in a similar way; however, these cells were more resistant to concentrations of menadione exceeding 15 μg · cm^{-3} than the cells of the wild strain. The cells grown on raffinose, a non-fermentable carbon source showed a similar sensitivity to menadione as the cells of the wild strain grown on glucose.

Discussion

The resistance of an organism to harmful effects of environmental substances depends on the efficiency of adaptative response and on constitutive resistance. Adaptative response involves increased efficiency of cell repair and defence mechanisms due to an environmental stress response inducted by an external stimulus. In stress response to menadione transcription factors, such as Hsf1p, Msn2/4p, Skn7p, Yap1p act as agents; these agents activate the transcription of the respective target genes [18–20]. These genes code: heat shock proteins, chaperones, cell wall proteins, metabolic enzymes, components of ubiquitin-proteasome degradation pathway and proteins that intercept and scavenge reactive oxygen species among others. The phenomenon of resistance or cross-protection is a physiological symptom of response to the shock induced by menadione. Studies by Castro et al [4] and Flatery-O'Brien et al [21] showed the appearance of resistance to lethal concentrations of menadione after a preincubation of the yeast cells of wild strain and its mutants in the presence of low menadione concentrations. Using an respiratory deficient strain, it was found that functional mitochondria were needed for conferring full resistance to menadione, but that induction of the adaptative response did not depend on mitochondrial function. Studies by Fernendes et al [22] proved that the cells treated with sublethal concentrations of menadione exhibited cross-protection to lethal doses of peroxide, indicating that menadione response encompasses H_2O_2.

Enhancement of resistance to menadione as a result of adaptive stress response is less significant for the viability of cells than constitutive resistance. The ability to convert superoxide anion into molecular oxygen and hydrogen peroxide, which is further eliminated by either catalase or peroxidases, is crucial to tolerance to menadione.

Earlier studies have shown that the deletion of SOD1 gene and both the SOD1, SOD2 genes, encoding superoxide dismutase produced high sensitivity to menadione treatment [5, 23]. As a result of adaptative response the resistance of these mutants to menadione increased but the absence of superoxide dismutase enzyme was still observed, since mutants showed a higher sensitivity than the wild strains [3].

In this study menadione was constantly present in the environment in which the cells grew and this is why, while analyzing the level of sensitivity of cells to this substance the mechanisms independent of stress response should also be taken into account. Such mechanisms include those which are connected with the genetic organization of antioxidant system or with metabolic ability of these cells.

The respiratory deficient cells (*rho*$^-$ mutants) were characterized by higher resistance to larger concentrations of menadione than the cells of the wild strain in conditions of glucose repression (Table 1). In both cases the cells metabolized glucose by fermentation. As by other studies shown, the mitochondrial status affects cell survival after treatment with oxidants. According to Rasmussen et al [24] the cells of respiratory mutant complete loss of the mitochondrial genome (*rho*^{0}) were characterized by a higher survival rate than the cells of the wild strain in the presence of 4-nitroquinoline-1-oxide (4-NQO), a compound acting on the cell membrane as its main target. Similar results were obtained by Blaszczynski et al [25], after application of paraquat, a redox active drug known to generate superoxide anions in mitochondria and cytosol of yeast. These authors observed then that the resistance of the cells of respiratory mutant was higher than the resistance of isogenic cells of the wild strain. Similar resistance was caused by lowering respiration by physiological mechanisms, as well as by some inhibitors of electron transfer chain of mitochondria.

The dysfunction of mitochondria manifested as lack of activity of the respiratory chain seems to be a key issue also for the emergence of resistance to sodium nitrate(V), salinity, iron salts and to the atmosphere containing 100 % of oxygen [26–29]. Probably, most of these eliminating the mitochondria which are the main source of reactive oxygen species (ROS) [24, 30] may reduce the harmful effects of the analyzed substances both under physiological and stress conditions.

Under the conditions of full activity of respiration pathway induced by the presence of ethanol yeast cells proved to be extremely sensitive to menadione. Mitochondria are the primary cellular source of ROS. In *S. cerevisiae* cells, external mitochondrial NADH dehydrogenases [31], coenzyme Q [32] and succinate dehydrogenase [33] were identified as the sites of ROS production. Additionally, mutations or drugs that block terminal steps of the respiratory chain further increase ROS generation due to the accumulation of reduced electron carriers [34, 35]. The maintenance of a stable respiratory chain strongly prevents the generation of mitochondrial ROS [36]. Studies by O'Brien et al [37] confirm that during late stationary phase, when intensive respiration occurs, the levels of carbonylated mitochondrial proteins increased in wild strains and in *sod1* and *sod2* mutants. However, it should be said that in the logarithmic and early-stationary phases of growth, using protein carbonylation as a measure of oxidative modification no correlation was found between the overall levels of respiration and the concentration of oxidatively damaged mitochondrial proteins in parental either single or double SOD mutants [37].

Unexpectedly, the cells grown in raffinose based media – a poor fermentable carbon source – proved to be more resistant to the toxic influence of menadione than the cells grown on ethanol. Probably most differences in the sensitivity of these cells are connected with the metabolic status of their mitochondria. Similarly, Knorre et al [38] observed that the cells pre-grown in raffinose-based media have low-energized mitochondria, unlike the cells grown in the glycerol-based media. This is why the cells pre-grown in raffinose based media, unlike the cells grown in the glycerol, are resistant to acetate induced ROS formation and dead. It was also found, that the mitochondria of the cells grown on raffinose are additionally protected from harmful effects caused by ROS. Under these conditions the formation of peroxisomes is depresed and peroxisomal catalase A could be localized to the mitochondrial matrix [39].

Conclusions

The toxicity of menadione is connected not only with the efficiency of cell adaptative response and constitutive resistance including antioxidant defence mechanisms but also depends on the type of energetic metabolism of yeast cells.

The yeast cells grown on fermentative substrate glucose and on poor fermentative raffinose were more resistant to menadione than the cells grown on oxidative substrate ethanol.

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METABOLIZM ENERGETYCZNY KOMÓREK DROŻDŻY *Saccharomyces cerevisiae* A TOKSYCZNOŚĆ MENADIONU

Katedra Biochemii i Chemii Środowiskowej, Wydział Nauk Rolniczych
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Menadion (2-metylo-1,4 naftochinon) jest powszechnie stosowanym w praktyce laboratoryjnej czynnikiem prooksydacyjnym. Generuje oksydacyjne uszkodzenia makromolekuł komórkowych. Wyniki wcześniejszych badań wskazują, że sprawność systemu antyoksydacyjnego jest bardzo ważna w ochronie komórek drożdżowych przed toksycznymi efektami indukowanymi menadionem. Celem prezentowanej pracy było określenie wrażliwości komórek drożdży *Saccharomyces cerevisiae* o różnym metabolizmie energetycznym na menadion. W badaniach wykorzystano komórki szczepu dzikiego SP4 oraz jego izogenicznego mutanta oddechowego SP4 *rho*$^-$. Hodując drożdże w pożywkach zwierających różne źródła węgla (ulegające fermentacji i nie ulegające fermentacji), uzyskano komórki o różnej aktywności oddechowej. Poziom przeżywalności komórek drożdży oznaczono poprzez liczenie kolonii wyrosłych na pożywkach stałych w obecności tego prooksydantu.

W warunkach pełnej aktywności oddechowej drożdży w obecności nie ulegającego fermentacji źródła węgla, jakim jest etanol, zanotowano większą wrażliwość komórek drożdży na menadion niż w warunkach represji układu oddechowego (pożywka zawierająca 2 % lub 10 % glukozę), w przypadku komórek mutanta niezdolnego do oddychania tlenowego oraz w obecności słabo fermentowalnego źródła węgla jakim jest rafinoza.

Uzyskane wyniki sugerują, że toksyczność menadionu jest związana nie tylko ze sprawnością komórkowych mechanizmów antyoksydacyjnych, ale także zależy od typu metabolizmu energetycznego komórek drożdży.

Słowa kluczowe: menadion, drożdże, metabolizm energetyczny

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Mirosław WYSZKOWSKI[1], Jadwiga WYSZKOWSKA[2]
and Maja RADZIEMSKA[1]

MACROELEMENT CONTENT IN YIELD OF OATS (*Avena sativa* L.) CULTIVATED ON SOILS CONTAMINATED WITH COPPER, ZINC, TIN, COBALT AND MANGANESE

ZAWARTOŚĆ MAKROPIERWIASTKÓW W PLONIE OWSA (*Avena sativa* L.) UPRAWIANEGO NA GLEBACH ZANIECZYSZCZONYCH MIEDZIĄ, CYNKIEM, CYNĄ, KOBALTEM I MANGANEM

Abstract: The aim of study was to compare the effect of contamination of soil with copper, zinc, tin, cobalt and manganese applied in the following doses: 0 (control), 20, 40, 80, 120, 240 and 480 mg · kg^{-1} of soil on macroelement content in the aboveground parts of oats (*Avena sativa* L.). The effect of heavy metals on macroelement content in oats depended both on the element and on its dose. The greatest changes were observed in calcium content. Copper increased the content of magnesium, nitrogen and, more than others, calcium, in the aboveground parts of oats. A similar relationship was observed for phosphorus, potassium and sodium, but only after relatively low doses of copper were applied; the effect of high doses was distinctly negative. Contamination of soil with high doses of zinc increased the content of phosphorus, but not nitrogen, sodium, magnesium, potassium or calcium, in oats. Tin favoured the accumulation of sodium and, when applied in low doses, also phosphorus, nitrogen and calcium, in plants; in addition, it reduced the content of magnesium and potassium in oats. Cobalt had a significantly negative effect on potassium content in the aboveground parts of oats and on the other hand positively affected the content of phosphorus, sodium, magnesium and, especially, calcium. Manganese generally increased the accumulation of the macroelements under study in plants, but its higher doses reduced the content of sodium and, partly, potassium and magnesium. A strong effect of soil contamination with heavy metals on content of some macroelements in oats was connected with toxic impact of copper, cobalt and, in a smaller degree, manganese on the growth and development of plants.

Keywords: contamination, copper, zinc, tin, cobalt, manganese, oats yield, macroelements content

Contamination of the environment with trace elements in Poland is generally observed in small areas, but locally it may cause some problems, eg in plant cultivation

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[1] Department of Environmental Chemistry, University of Warmia and Mazury, 10–727 Olsztyn, pl. Łódzki 4, Poland, phone./fax 89 523 3566, email: miroslaw.wyszkowski@uwm.edu.pl

[2] Department of Microbiology, University of Warmia and Mazury, 10–727 Olsztyn, pl. Łódzki 3, phone/fax +48 89 523 3566.

[1]. Copper, zinc and manganese are elements which, in small amounts, are necessary for the correct function of organisms [2]. Plants may tolerate elevated concentrations of metals in soil, but their high concentrations are harmful, both to plants and to other organisms [3]. Excessively high metal concentrations may cause stress reactions in plants, depending on the species and on many other factors, mainly the soil properties (interactions between trace elements are of considerable importance) [4]. At the same time, contamination of soil with the elements favours contamination of plants and incorporating them in subsequent links of the trophic chain [5], which in consequence results in their excessive content in food of plant (and sometimes of animal) origin [6]. They cause numerous disorders of various elements' (both macro- and microelements) uptake by plants and of plant growth and development.

Therefore, the aim of a study was to compare the effect of contamination of soil with copper, zinc, tin, cobalt and manganese on macroelement content in the aboveground parts of oats (*Avena sativa* L.).

Material and methods

A vegetative pot experiment was performed in 4 replications in the vegetation hall of the University of Warmia and Mazury in Olsztyn on slightly acidic soil with the granulometric composition of loamy sand, in polyethylene pots. The soil had the following characteristics: pH_{KCl} – 6.9; hydrolytic acidity (HA) – 15.38 mmol $(H^+) \cdot kg^{-1}$; exchangeable basic cations (EBC) – 98.50 mmol(+) $\cdot$ kg^{-1}; cation exchange capacity (CEC) – 113.88 mmol(+) $\cdot$ kg^{-1}; base saturation (BS) – 86.50 %; organic C content – 6.35 g $\cdot$ kg^{-1}. The examined factors included heavy metals: copper ($CuCl_2$), zinc ($ZnCl_2$), tin ($SnCl_2 \cdot 2H_2O$), cobalt ($CoCl_2 \cdot 6H_2O$) and manganese ($MnCl_2 \cdot 4H_2O$) applied in the following doses: 0 (control), 20, 40, 80, 120, 240 and 480 mg $\cdot$ kg^{-1} of soil. Macro- and microelements were added to all the objects in the following amounts, in mg $\cdot$ kg^{-1} of soil, converted to a pure component: N – 120 ($CO(NH_2)_2$), P – 42 (K_2HPO_4), K – 120 (K_2HPO_4 + KCl), Mg – 20 ($MgSO_4 \cdot 7H_2O$), Mo – 5 ($Na_2MoO_4 \cdot 2H_2O$) and B – 0.33 (H_3BO_3); the following were added to selected ones: Zn – 5 ($ZnCl_2$), Cu – 5 ($CuSO_4 \cdot 5H_2O$), Mn – 5 ($MnCl_2 \cdot 4H_2O$). The dose of zinc, copper and manganese at 5 mg $\cdot$ kg^{-1} of soil was applied in those variants where soil was not contaminated with increasing doses of the metals. The examined elements, as well as macro- and micro-elements as aqueous solutions were thoroughly mixed with soil (3.2 kg) and placed in the pots. The effect of the metals was tested on oats (*Avena sativa* L.), 'Borowik' c.v. The experiment, at a density of 12 oats plants per pot, was conducted for 65 days, until the ear formation phase in which the plants were harvested and samples were taken for laboratory analyses. During the experiment, the soil humidity was kept at 60 % of the capillary capacity.

Samples of plant material were cut, dried and ground. The nitrogen content was determined by the Kjeldahl method, phosphorus – by the vanadium-molybdenum method, potassium, calcium and sodium – by atomic emission spectrometry (AES) and magnesium – by atomic absorption spectrometry (AAS). Statistical analysis was performed with the Statistica software pack [7].

Results and discussion

Macroelement content in plants was affected by the metal (Tables 1 and 2). The greatest changes were observed with calcium content.

Table 1

The content of nitrogen, phosphorus and potassium
in aboveground parts of oats (*Avena sativa* L.) [g · kg^{-1} d.m.]

Dose [mg · kg^{-1} of soil]	Cu	Zn	Sn	Co	Mn
Nitrogen (N)					
0	6.91	7.83	7.83	7.83	7.83
20	8.10	8.79	6.89	5.20	9.70
40	9.71	12.62	7.83	6.61	9.09
80	7.74	6.32	9.88	6.89	9.13
120	8.06	5.63	9.49	10.67	8.32
240	8.62	6.82	8.32	n.a.	8.47
480	8.97	6.28	6.35	n.a.	8.70
Average	8.30	7.76	8.09	7.44	8.75
LSD	a – 1.11*; b – 1.31*; a · b – 2.83**				
Phosphorus (P)					
0	4.61	4.61	4.61	4.61	4.61
20	5.40	5.18	7.03	5.35	6.63
40	5.26	5.81	8.73	5.64	5.91
80	5.06	5.12	6.99	5.21	8.54
120	4.87	5.46	7.23	5.48	8.74
240	3.41	5.75	6.91	n.a.	8.32
480	2.36	6.60	6.71	n.a.	6.52
Average	4.43	5.50	6.89	5.26	7.04
LSD	a – 0.34**; b – 0.40**; a · b – 0.87**				
Potassium (K)					
0	18.09	18.09	18.09	18.09	18.09
20	20.65	21.74	17.29	19.20	18.69
40	18.85	22.45	18.36	19.57	20.32
80	18.31	21.14	18.19	18.76	18.34
120	17.49	19.58	16.80	15.41	18.13
240	16.58	21.00	17.61	n.a.	18.29
480	14.70	20.80	15.85	n.a.	17.41
Average	17.81	20.69	17.45	18.21	18.47
LSD	a – 1.20**; b – 1.41**; a · b – n.s.				

Explanations for Tables 1 and 2: LSD significant for: a – metal, b – metal dose; *$p \le 0.05$; **$p \le 0.01$; n.s. – non-significant; n.a. – not analysed because of an insufficient amount of plant material.

Table 2

The content of sodium, magnesium and calcium
in aboveground parts of oats (*Avena sativa* L.) [g $\cdot$ kg^{-1} d.m.]

Dose [mg $\cdot$ kg^{-1} of soil]	Cu	Zn	Sn	Co	Mn
Sodium (Na)					
0	1.31	1.31	1.31	1.31	1.31
20	1.38	1.49	1.95	1.20	2.60
40	1.38	2.20	2.03	1.45	2.70
80	1.59	1.06	2.15	1.68	2.20
120	1.31	1.16	1.85	1.64	1.97
240	1.21	1.40	2.22	n.a.	1.73
480	1.11	0.81	2.50	n.a.	1.16
Average	1.33	1.35	2.00	1.46	1.95
LSD	a – 0.16**; b – 0.18**; a $\cdot$ b – 0.40**				
Calcium (Ca)					
0	2.61	2.61	2.61	2.61	2.61
20	2.93	4.45	4.77	4.40	5.51
40	2.80	8.29	6.33	6.53	6.15
80	3.01	3.50	6.90	7.23	6.08
120	5.16	4.30	5.83	12.33	6.24
240	5.50	5.40	5.14	n.a.	7.34
480	10.10	5.63	4.53	n.a.	7.61
Average	4.59	4.88	5.16	6.62	5.93
LSD	a – 0.47**; b – 0.55**; a $\cdot$ b – 1.20**				
Magnesium (Mg)					
0	2.00	2.00	2.00	2.00	2.00
20	2.05	2.23	1.67	2.22	2.10
40	2.01	2.12	1.96	2.37	2.12
80	2.25	2.00	2.16	2.17	1.85
120	2.08	1.96	1.66	2.93	1.84
240	2.21	1.92	1.75	n.a.	1.75
480	2.39	1.55	1.71	n.a.	2.12
Average	2.14	1.97	1.84	2.34	1.97
LSD	a – 0.13**; b – 0.15**; a $\cdot$ b – 0.32**				

Explanations see Table 1.

Copper caused an increase in magnesium, nitrogen, and – more than others – calcium content in the aboveground parts of oats (Tables 1 and 2). Following the application of the highest dose of copper – 480 mg Cu $\cdot$ kg^{-1} of soil, the observed increase was as follows, as compared with the control object: magnesium 20 %, nitrogen 30 % and calcium 287 %. A similar relationship was shown to exist for phosphorus, potassium and sodium, but only following the application of small doses of copper; the effect of high doses was always negative. The content of the elements in oats in the object with the highest copper contamination was lower than in the control by 49 %, 19 % and 15 %, respectively.

Contamination of soil with high doses of zinc increased the phosphorus content in oats, but not that of nitrogen, sodium, magnesium, potassium or calcium (Tables 1 and 2). Contamination of soil with zinc at 480 mg Zn · kg^{-1} of soil increased the phosphorus content in the aboveground parts of oats by 43 %. Low doses of zinc increased the contents of the other macroelements, whereas high doses decreased the content of nitrogen, sodium, magnesium, potassium and calcium. It should be noted that the potassium and calcium content, even in the object with the highest dose of zinc (480 mg Zn · kg^{-1}), was higher than in the control object.

Tin favoured the accumulation of sodium and small amounts of phosphorus, nitrogen and calcium in plants, but it reduced the content of magnesium and potassium in oats (Tables 1 and 2). It is noteworthy that a linear increase was observed only in the sodium content which was higher by 91 % with 480 mg Sn · kg^{-1} as compared with the control object. The accumulation of phosphorus, nitrogen and calcium in the aboveground parts of oats was maximal with 40, 80 and 80 mg Sn · kg^{-1} of soil, respectively, whereas a higher contamination with tin reduced their content as compared with objects with lower doses of Sn. The highest dose of tin (480 mg Sn · kg^{-1} of soil) produced a relatively small, but significant, decrease in potassium and magnesium content in the aboveground parts of oats. The decrease was 12 % for potassium and 15 % for magnesium content.

Cobalt had a negative effect on potassium content in the aboveground parts of oats and a positive effect on the content of phosphorus, sodium, magnesium and, especially, calcium (Tables 1 and 2). The decrease in potassium content was relatively small, by 15 %, while the phosphorus content increased by 19 %, that of sodium – by 25 %, magnesium – by 47 %, and calcium – by as much as 372 %. The nitrogen content fluctuated. However, it should be added that the changes were related to the doses ranging from 0 to 120 mg Co · kg^{-1} of soil, as higher doses of cobalt were toxic to plants, making it impossible to obtain a sufficient mass of plants for chemical analyses.

Manganese generally increased the accumulation of the examined macroelements in plants, but its higher doses restricted the content of sodium and partly potassium and magnesium (Tables 1 and 2). The highest content of nitrogen in the aboveground parts of oats was determined in the soil contaminated with 20 mg Mn · kg^{-1}, that of potassium, sodium and magnesium – 40 mg Mn · kg^{-1}, phosphorus – 120 mg Mn · kg^{-1}; only the content of calcium increased until the dose of manganese was 480 mg Mn · kg^{-1}. Of all the macroelements, the growth of calcium content was the strongest – nearly three-fold in relation to the object without manganese. The highest manganese dose (480 mg Mn · kg^{-1} of soil) decreased the content of most macroelements in oats, but only in the case of sodium and potassium was it lower than in the control variant.

Contamination of soil with heavy metals has a strong effect on content of some macroelements in oats. This effect correlated with toxic impact on the growth and development of plants, which causes a decrease in their mass, especially in objects with copper, cobalt, in a smaller degree with manganese (Fig. 1). Contamination of soil with zinc and tin resulted in relatively small changes of the aboveground parts mass. The highest dose (480 mg · kg^{-1} of soil) of copper, cobalt and manganese caused 94, 99 and 35 % reduction of the mass of aboveground parts of oats, compared with the variant without heavy metals application.

Other authors [2–4, 8–14] have pointed out that trace elements have a strong and varied effect on the macroelement content in plants, which has been confirmed in the author's own study. In an experiment conducted by Eleiwa [8] copper strongly affected nitrogen

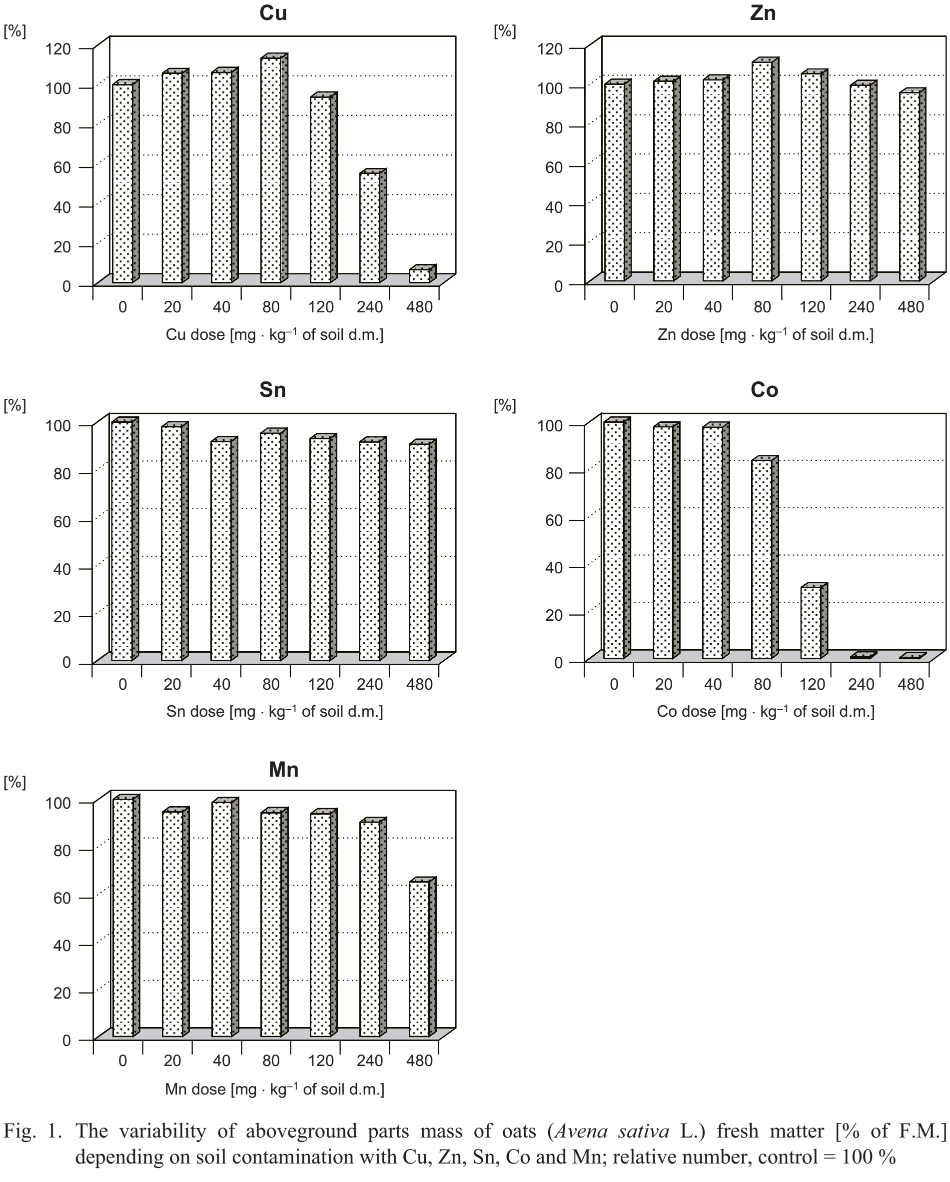

Fig. 1. The variability of aboveground parts mass of oats (*Avena sativa* L.) fresh matter [% of F.M.] depending on soil contamination with Cu, Zn, Sn, Co and Mn; relative number, control = 100 %

assimilation in wheat and lupine. Copper and zinc also reduced nitrogen, sodium, potassium and calcium content in plants and, to a lesser degree, they affected phosphorus and magnesium content. Contamination of soil with copper may result in a nitrogen content increase in spring barley [3].

According to Sienkiewicz-Cholewa and Wrobel [9], copper determines a good supply of nitrogen to plants as it takes part in nitrogen compound transformations. Copper can also have an antagonistic effect on other elements [3]. Zinc is one of the mobile elements in the soil [10]. Zinc can also increase nitrogen content in plants [11], whereas the effect of cobalt on nitrogen content is a result of its participation in nitrogen fixation, where it is a component of a coenzyme, although this only regards the papilionaceous plants [2]. Trace elements, particularly copper and zinc and, to a lesser extent, tin, manganese and cobalt, especially when applied in low and medium doses, favour the accumulation of nitrogen in some plants, eg in spring barley [12]. The findings of experiments conducted by Parker [13] and Kitaeva [14] indicate that growing contamination of soil with zinc may decrease phosphorus content in plants. According to Kozera et al [4], copper may decrease potassium content and increase that of calcium, while zinc favours accumulation of sodium in potato tubers. In the study conducted by Wyszkowski and Wyszkowska [3] and by Wyszkowski et al [12], copper increased the content of calcium, sodium, magnesium and potassium, but not phosphorus, in spring barley. According to Kabata-Pendias and Pendias [2], there is an antagonism between copper and calcium and between zinc and magnesium. The findings of an experiment conducted by Wyszkowski et al [12] indicate that zinc may increase the content of calcium, magnesium, potassium and partly phosphorus and sodium in plants. High doses of zinc decreased phosphorus and sodium content in spring barley, whereas tin increased the accumulation of calcium and decreased magnesium content.

Conclusions

1. The effect of heavy metals on macroelement content in oats depended both on the element and on its dose. The greatest changes were observed in calcium content.
2. Copper increased the content of magnesium, nitrogen and, more than others, calcium, in the aboveground parts of oats. A similar relationship was observed for phosphorus, potassium and sodium, but only after relatively low doses of copper were applied; the effect of high doses was distinctly negative.
3. Contamination of soil with high doses of zinc increased the content of phosphorus, but not nitrogen, sodium, magnesium, potassium or calcium, in oats.
4. Tin favoured the accumulation of sodium and, when applied in low doses, also phosphorus, nitrogen and calcium, in plants; in addition, it reduced the content of magnesium and potassium in oats.
5. Cobalt had a significantly negative effect on potassium content in the aboveground parts of oats and a positive effect on the content of phosphorus, sodium, magnesium and, especially, calcium.

6. Manganese generally increased the accumulation of the macroelements under study in plants, but its higher doses reduced the content of sodium and, partly, potassium and magnesium.

7. A strong effect of soil contamination with heavy metals on content of some macroelements in oats was correlated with toxic impact of copper, cobalt and, in a smaller degree, manganese on the growth and development of plants.

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ZAWARTOŚĆ MAKROPIERWIASTKÓW W PLONIE OWSA (*Avena sativa* L.) UPRAWIANEGO NA GLEBACH ZANIECZYSZCZONYCH MIEDZIĄ, CYNKIEM, CYNĄ, KOBALTEM I MANGANEM

Katedra Chemii Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Celem przeprowadzonych badań było określenie wpływu zanieczyszczenia gleby miedzią, cynkiem, cyną, kobaltem i manganem w dawkach 0 (kontrola), 20, 40, 80, 120, 240 i 480 mg · kg^{-1} gleby na zawartość makroelementów w częściach nadziemnych owsa (*Avena sativa* L.). Na zawartość makroelementów w roślinach, oprócz poziomu zanieczyszczenia, duży wpływ miał rodzaj metalu. Oddziaływanie metali ciężkich na zawartość makroelementów w owsie było związane z poszczególnymi pierwiastkami i ich dawkami. Największe zmiany zaobserwowano w zawartości wapnia. Miedź wywołała zwiększenie zawartości magnezu, azotu i w największym stopniu wapnia w częściach nadziemnych owsa. Podobną zależność wykazano w przypadku fosforu, potasu i sodu, ale tylko po zastosowaniu niewielkich dawek miedzi, podczas gdy duże dawki działały zdecydowanie ujemnie. Zanieczyszczenie gleby dużymi dawkami cynku spowodowało wzrost zawartości fosforu w owsie, w odróżnieniu od azotu, sodu, magnezu, potasu i wapnia. Cyna sprzyjała nagromadzaniu sodu, a w niewielkich dawkach także fosforu, azotu i wapnia w roślinach, jednocześnie ograniczała zawartość magnezu i potasu w owsie. Kobalt działał wyraźnie ujemnie na zawartość potasu w częściach nadziemnych owsa, a dodatnio na zawartość fosforu, sodu, magnezu i szczególnie wapnia. Mangan na ogół powodował zwiększenie nagromadzania w roślinach badanych makropierwiastków, jednakże większe jego dawki ograniczały zawartość sodu oraz częściowo potasu i magnezu. Silny wpływ zanieczyszczenia gleby metalami ciężkimi na zawartość niektórych makroelementów w owsie był skorelowany z toksycznym oddziaływaniem miedzi, kobaltu i, w mniejszym stopniu, manganu na wzrost i rozwój roślin.

Słowa kluczowe: zanieczyszczenie, miedź, cynk, cyna, kobalt, mangan, plon owsa, zawartość makroelementów

Varia

INVITATION FOR ECOPOLE '09 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 18th annual Central European Conference ECOpole '09, which will be held in **14–17 X 2009** (Thursday–Saturday) on Wilhelms Hill at Uroczysko in Piechowice, PL.

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

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

On the first day the debates of sections SI and SII will take place. The second day will be started with an ecological excursion. Afterwards the plenary Session with lectures on **environmental education** as well as **grants within the EU Programmes** and presentation of **EU Centres of Excellence** will be held. Then the **Forum of Young Scientists** – the presentation (lectures and posters) of young scientists work will take place.

The main topic of the third day is the influence of environment quality on the **human health**.

During the Conference an exhibition of publications concerned with conference topics will be also organised.

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format)
- extended abstracts (4–6 pages) in the semi-annual *Proceedings of ECOpole*;

full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.).

Additional information one could find on the Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **31.08.2009** and for the Extended Abstracts: **1.10.2009**. The actualised list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one will find (starting from 15.07.2009) on the Conference website.

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

The Conference fee is 300 € (covering hotel, meals and transportation during the Conference). It could be reduced (to 170 €) for young people actively participating in the Forum of Young Scientists. But the colleague has to deliver earlier the Extended Abstract (4-6 pages) of his/her contribution (deadline is on 15.08.2009), and a recommendation of his/her Professor.

Fees transferred after 15.09.2009 are 10% higher.

At the Reception Desk each participant will obtain a CD-ROM with abstracts of the Conference contributions as well as Conference Programme (the Programme will be also published on the Conference website).

Further information is available from:
Dr hab. Maria Wacławek, prof. UO
Chairperson of the Organising Committee
of ECOpole ’09 Conference
University of Opole
email: Maria.Waclawek@uni.opole.pl
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ZAPRASZAMY
DO UDZIAŁU W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI
ECOpole ’09
w dniach 14–17 X 2009

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

Będzie to osiemnasta z rzędu konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w ośrodku „Uroczysko” na Wzgórzu Wilhelma w Piechowicach. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego.

Obrady konferencji ECOpole ’09 będą zgrupowane w pięciu sekcjach:

- **SI Chemiczne substancje w środowisku przyrodniczym oraz ich monitoring;**
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- **SIII Zarządzanie środowiskiem w warunkach kryzysowych**;
- **SIV Forum Młodych (FM) i Edukacja prośrodowiskowa**;
- **SV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi**.

Materiały konferencyjne będą opublikowane w postaci:

- abstraktów (0,5 strony formatu A4) na CD-ROM-ie;
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- artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (*Ecol. Chem. Eng.*) oraz niektórych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*.

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa + wydruk) planowanych wystąpień upływa w dniu 31 sierpnia 2009 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2009 r. na stronie webowej konferencji

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Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł w języku polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami stawianymi artykułom drukowanym w czasopiśmie *Ecological Chemistry and Engineering*, które jest dostępne w wielu bibliotekach naukowych w Polsce i zagranicą. Są one takie same dla prac drukowanych w półroczniku *Chemia – Dydaktyka – Ekologia – Metrologia*. Zalecenia te są również umieszczone na stronie webowej konferencji.

Koszt uczestnictwa w całej konferencji wynosi 1000 zł i pokrywa opłatę za udział, koszt noclegów i wyżywienia oraz rocznej prenumeraty Ecol. Chem. Eng. (razem blisko 2000 ss.) łącznie z materiałami Konferencji. Jest możliwość udziału tylko w jednym wybranym przez siebie dniu, wówczas opłata wyniesie 650 zł i będzie upoważniała do uzyskania wszystkich materiałów konferencyjnych, jednego noclegu i trzech posiłków (śniadanie, obiad, kolacja), natomiast osoby zainteresowane udziałem w dwóch dniach, tj. w pierwszym i drugim lub drugim i trzecim, winny wnieść opłatę w wysokości 800 zł. Opłata dla magistrantów i doktorantów oraz młodych doktorów biorących aktywny udział w Forum Młodych może być zmniejszona do 600 zł, przy zachowaniu takich samych świadczeń. Osoby te winny dodatkowo dostarczyć: rozszerzone streszczenia (4–6 stron) swoich wystąpień (**do 15.08.2009 r.**). Jest także wymagana opinia opiekuna naukowego. Sprawy te będą rozpatrywane indywidualnie przez Radę Naukową oraz Komitet Organizacyjny Konferencji. Członkowie Towarzystwa Chemii i Inżynierii Ekologicznej i Polskiego Towarzystwa Chemicznego (z opłaconymi na bieżąco składkami) mają prawo do obniżonej opłaty konferencyjnej o 25 zł. Opłaty wnoszone po dniu 15 września 2009 r. są większe o 10% od kwot podanych powyżej. Wszystkie wpłaty winne być dokonane na konto w Banku Śląskim:

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15th ICHMET

15th International Conference on Heavy Metals in the Environment
September 19–23, 2010
Gdańsk, Poland

Organized by
Chemical Faculty, Gdańsk University of Technology (GUT)
together with
Committee on Analytical Chemistry of the Polish Academy Sciences (PAS)

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- Soil quality criteria
- Remediation technologies
- Control strategies for heavy metal emissions and deposition
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- Nutrient-metal interactions
- Advancements in analytical tools (procedures and measurement devices)

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- Heavy metals in foods
- Impact of global change on heavy metal cycle

For further information on the conference, please contact:

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Przypisy i tabele podobnie jak rysunki zapisujemy jako osobne pliki.

Literaturę prosimy zamieszczać wg poniższych przykładów:

[1] Kowalski J. and Malinowski A.: Polish J. Chem. 1990, **40**, 2080–2085.

[2] Nowak S.: Chemia nieorganiczna, WNT, Warszawa 1990.

[3] Bruns I., Sutter K., Neumann D. and Krauss G.-J.: *Glutathione accumulation – a specific response of mosses to heavy metal stress*, [in:] Sulfur Nutrition and Sulfur Assimilation in Higher Plants, P. Haupt (ed.), Bern, Switzerland 2000, 389–391.

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Halina Szczegot

SKŁAD KOMPUTEROWY
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