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Czesława JASIEWICZ[1], Małgorzata SZCZERBIŃSKA-BYRSKA[2]
and Agnieszka BARAN[1]

LEGAL AND ORGANIZATIONAL PROBLEMS OF REALIZATION OF "PROGRAMME FOR THE DISPOSAL OF ASBESTOS AND ASBESTOS-CONTAINING PRODUCTS IN POLAND"

PRAWNO-ORGANIZACYJNE PROBLEMY REALIZACJI „PROGRAMU USUWANIA AZBESTU I WYROBÓW ZAWIERAJĄCYCH AZBEST NA TERYTORIUM POLSKI"

Abstract: After the introduction dealing with the occurrence, application and harmfulness of asbestos, the paper presents basic legal regulations concerning the use and disposal of asbestos-containing products. The main assumptions of "Programme for the disposal of asbestos and asbestos-containing products in Poland" were discussed. The assessment of the programme implementation was presented on the basis of inspection report prepared by the Ministry of Economy and NIK (Supreme Chamber of Control).

Keywords: asbestos, pathogenic effect of asbestos, legal regulations

Occurrence and application of asbestos

Asbestos is a commercial name of a group of fibrous materials. In chemical terms these are hydrated silicates of magnesium, iron, calcium and sodium. There are following types of asbestos: chrysotile (fibrous variety of serpentine, ie hydrated silicate of magnesium), amosite (silicate of iron and magnesium), crocidolite (silicate of sodium and iron) and anthophyllite (magnesium silicate containing iron). Despite the fact that asbestos occurrence in nature is quite common, it is exploited on industrial scale only in several places in the world. There are asbestos deposits in Poland, which could be exploited for industry. Asbestos properties, such as high resistance to high and low temperatures, small heat conductivity and resistance to chemicals caused that it became widely used as a valuable raw material, also in Poland. Asbestos was commonly used in

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

[2] Administration with Economics Department, Higher Vocational School in Tarnow, ul. A. Mickiewicza 8, 33–100 Tarnów, Poland.

several sectors of the economy, primarily in construction industry, but also in power industry, transport and chemical industry. The applications of asbestos comprise:

– asbestos and cement products manufactured of chrisotile and amphibole asbestos, which include: roof tiles, pressure pipes, lining and elevation panels containing between 10 and 35 % of asbestos,

– insulation products used for insulation of steam boilers, heat exchangers, pipe coverings and fireproof clothing and fabrics; depending on the designation these contain between 75 and 100 % asbestos, mainly chrysotile,

– caulks: asbestos cardboard, asbestos-rubber plates and pleated packing,

– friction products, such as friction linings and brake linings used for various types of brakes,

– textiles: ropes and mats,

– hydroinsulation products: asphalt pitch, sealing putties, refined asphalt, cementitious mortar formulations, building paper, floor tiles containing between 20 and 40 % of asbestos.

It has been estimated that flat and corrugated asbestos plates constitute ca 96 % of total amount of asbestos containing products. Production of asbestos-cement plates in Poland started in 1907 in Krakow, then about 1910 in Lubliniec and Ogrodzieniec near Zawiercie (ca 1920). However, in Poland asbestos started to be used in construction works on a wide scale in the sixties of the previous century, when 4 large plants manufacturing asbestos and cement products were put into operation. Production of asbestos-cement plates in Poland was finally banned [1] by the act of 19 June 1997 on the "Prohibition of the use of asbestos-containing products" published in Journal of Laws 1997, No. 101, item 628 [2] and Journal of Laws 1998, No. 156, item 1018 [3] with later amendments. A ban on the turnover of asbestos and asbestos-containing products has been in force since 28 March 1999. On the basis of statistical data on the production, import and distribution of asbestos-cement products and assumed mean indices of their consumption, it was assessed that in 2000 there was 15466.5 thousand Mg asbestos containing products in Poland (Table 1).

Table 1

Predicted amount of asbestos containing wastes to be deposited in 2003–2032 [4]

Province	Years		
	2003–2012	2013–2022	2023–2032
	Amount of produced wastes [Mg]		
Dolnośląskie	201810	203640	144150
Kujawsko-pomorskie	277074	316656	197910
Lubelskie	773426	883916	552447
Lubuskie	83422	95340	59587
Łódzkie	406136	464156	290098
Małopolskie	329255	376292	235183
Mazowieckie	1036395	118445	740283
Opolskie	113998	130284	81428
Podkarpackie	232767	266020	166263

Table 1 contd.

Province	Years		
	2003–2012	2013–2022	2023–2032
	Amount of produced wastes [Mg]		
Podlaskie	386144	441308	275818
Pomorskie	204008	233152	145720
Śląskie	296057	311712	171511
Świętokrzyskie	303093	334964	199353
Warmińsko-mazurskie	229411	262184	163865
Wielkopolskie	355245	444056	310839
Zachodniopomorskie	185034	211468	132168
Poland	5413275	6186600	3866623

Pathogenic effect of asbestos

Pathogenic effect of asbestos occurs is result of inhalation of airborne fibres (which means that as long as the fibres are not released into the air they do not pose a hazard for health). Asbestos may be also present in water, beverages and food, from where it penetrates into the human organism. Currently, when manufacturing asbestos containing products was discontinued, the sources of this mineral remain as follows:

– improperly stored asbestos wastes, including so called illegal dumping sites, particularly in forests and open excavations,

– the use of asbestos products, which leads to air pollution with asbestos dust in result of corrosion and mechanical damage of asbestos-cement plates, abrasion of clutch plates and brake discs,

– unprofessional removal of asbestos containing panels from roofs or facades,

– heating, ventilation, air conditioning devices and insulation containing asbestos.

Asbestos becomes dangerous when it penetrates into the air as very small fibres, which are invisible to unaided human eye. Breathing in these fibres may cause one of the following diseases: asbestosis, ie scarring of the lung, lung cancer, mesothelioma. The health hazard depends on the type of asbestos, size of fibres and their concentration in the air, and the time of exposure. The gravest hazard is posed by respirable fibres, ie present in the air in a permanent form, which can penetrate to alveoli with the inhaled air. They are less than 3μm and are longer than 5 μm, however the most dangerous are fibres of ca 20 μm [5, 6].

Basic legal regulations concerning the handling and disposal of asbestos-containing products

Acts

1. *Act of 19 June 1997 on prohibition of the use of asbestos containing products* (Journal of Laws, 1997, No. 101, item. 628 with later amendments). The act prohibits

importing asbestos or asbestos containing products to the territory of Poland and the turnover of asbestos and asbestos containing products.

2. *Act of 7 July 1994 – Construction law* (Journal of Laws 1994, No. 89, item. 414 with later amendments), in pursuance of article 30, item 3 states that: a competent authority may impose, as a decision, an obligation to obtain permission to construct the object or carry out construction works, under obligation to fill the application as stated in item 1, if their realization may disturb the local plan of spatial management or pose a hazard to the safety of people or their property, deteriorate the state of the environment or cultural heritage, worsen the health- and sanitary conditions, introduce, fix or increase limitations or arduousness for the adjoining areas.

3. *Act of 27 April 2001 – Law on the environmental protection* (Journal of Laws 2001, No. 62, item 627 with later amendments). The law imposed on heads of communes, mayors and presidents of cities and other legal persons an obligation to supply information on the kind, amount and places of occurrence of substances (including asbestos) which pose particularly grave hazard to the environment.

4. *Act of 27April 2001 on wastes* (Journal of Laws 2001, No. 62, item 628 with later amendments). The act imposed among others an obligation on the producer of hazardous wastes (person involved in the disposal of asbestos containing products) to obtain the approval for hazardous asbestos containing waste programme granted by the appropriate governor of the province or local authority.

Regulations

1. *Regulation of the Minister of Environment of 27 September 2001 on the waste catalogue* (Journal of Laws 2001, No. 112, item 1206) places wastes containing asbestos on hazardous waste list in groups and sub-groups with appropriate classification codes.

2. *Regulation of the Minister of the Natural Environment of 9 October 2002 on the procedure of submitting information to the governor of province about the kind, amount and places of occurrence of substance posing particular hazards to the environment* (Journal of Laws 2002, No. 175, item 1439). The document states the deadlines and forms in which the information about the kind, amount and places where substances posing environmental hazard occur should be submitted.

3. *Regulation of the Minister of Economy of 30 October 2002 on the kinds of wastes which could be deposited non-selectively* (Journal of Laws 2002, No. 191, item 1595).

4. *Regulation of the Minister of Labour and Social Policy of 29 November 2002 on the highest permissible concentrations and rates of factors harmful to human health in the work environment* (Journal of Laws 2002, No. 217, item. 1933) states the highest tolerable concentrations of asbestos containing dusts in the work environment.

5. *Regulation of the Minister of the Natural Environment of 5 December 2002 on reference values for certain substances in the air* (Journal of Laws 2002, No. 1, item 12) determined the control limit concentrations of asbestos in the air.

6. *Regulation of the Minister of the Natural Environment of 24 March 2003 stating the detailed requirements for localisation, construction, operation and closure of*

particular types of landfills (Journal of Laws 2003, No. 61, item 549). The document states the requirements for deposition of asbestos containing wastes.

7. *Regulation of the Minister of the Infrastructure of 23 June 2003 on the information about the safety and protection of health and the plan of safety and protection of health* (Journal of Laws 2003, No. 120, item 1126) states the scope of construction works posing hazard for safety of health or people.

8. *Regulation of the Minister of Economy, Labour and Social Policy of 23 October 2003 on the requirements for the utilization and transport of asbestos and the use and cleaning the installations or appliances in which asbestos has been is present* (Journal of Laws 2003, No. 192, item 1876). The Regulation imposes an inventory duty on the owner or manager of places where asbestos has been or still is used. Such person is also obliged to submit annual reports to an appropriate head of commune, mayor or president of city. Legal entities submit the report to the governor of province.

9. *Regulation of the Minister of Economy, Labour and Social Policy of 2 April 2004 on the methods and conditions of safe use and disposal of asbestos containing products* (Journal of Laws 2004, No. 71, item 649) imposes an obligation on the owners or managers of objects, constructions, industrial installations or other asbestos containing sites of periodical checking the state of these products and preparation of an assessment of the state and potential use of asbestos containing products.

10. *Regulation of the Minister of Health of 1 December 2004 on substances, preparations or technological processes with carcinogenous or mutagenic effect in the work environment* (Journal of Laws 2004, No. 280, item 2771). The document states among others employer’s duties during works carried out in contact with harmful substances (including asbestos).

11. *Regulation of the Council of Ministers of 14 December 2004 on fees for using the environment* (Journal of Laws 2004, No. 279, item 2578).

12. *Regulation of the Minister of Health of 20 April 2005 on research and measurement of factors harmful for health in the work environment* (Journal of Laws 2005, No. 73, item 645). The document states among others the necessary test to be performed while working with harmful substances (including asbestos).

In compliance with the European legislation, bringing into circulation and application of products or substances containing asbestos was prohibited since January 2005 (Directive 1999/77/WE). Stricter regulations protecting workers against the risk of exposure to asbestos fibres have been in force since 15 April 2006 (Directive 2003/18/WE amending Directive 83/477/EWG) [4, 9–11].

Programme for the disposal of asbestos and asbestos containing products used in Poland

On 14 May 2002, the Council of Ministers of the Republic of Poland adopted the “Programme for the disposal of asbestos and asbestos containing products in Poland”. The programme spans a 30-year period of time, ie the years 2002–2032. The “Programme for the disposal of asbestos and asbestos containing products in Poland” was developed in result of:

– adoption by the Polish Parliament on 19 June 1997 a resolution on a programme of eliminating asbestos from the economy (The Polish Monitor 1997, No. 38, item 373) which called the Council of Ministers to among others develop a programme aimed at eliminating asbestos and asbestos containing products used on the territory of Poland,

– realization of the act of 19 June 1997 prohibiting the use of products containing asbestos (Journal of Laws 1997, No. 101, item 628; 1998, No. 156, item 1018; Journal of Laws 2000, No. 88, item 986; 2001, No. 100, item. 1085 and No. 154, item 1793) and the appropriate the executive provisions concerning this act.

It was assumed that the following measures will be taken over the thirty-year period of the programme implementation, ie from 2003 to 2032:

– implementation of legal regulations and standards on handling asbestos containing products used in the European Union,

– cleaning the territory of Poland of asbestos and eliminating asbestos containing products which have been in use for many years,

– disposal of asbestos wastes present on roads and squares owned by economic or other entities, including local governments,

– deposition of asbestos wastes on 84 landfills with area between 1 and 5 ha, located on the whole territory of Poland (Table 2),

– eliminating the negative health results in the inhabitants of Poland due to asbestos',

– liquidating asbestos environmental impact.

Table 2

Location of landfills for asbestos and cement wastes deposition in 2003–2032 [4]

Province	Years		
	2003–2012	2013–2022	2023–2032
	Number of landfills		
Dolnośląskie	2	1	1
Kujawsko-pomorskie	2	2	2
Lubelskie	3	3	1
Lubuskie	1	1	1
Łódzkie	3	2	2
Małopolskie	3	2	1
Mazowieckie	3	2	2
Opolskie	1	1	—
Podkarpackie	2	2	1
Podlaskie	2	1	2
Pomorskie	2	2	1
Śląskie	2	2	2
Świętokrzyskie	2	2	1
Warmińsko-mazurskie	2	2	1
Wielkopolskie	2	2	2
Zachodniopomorskie	2	2	1
Poland	34	29	21

The following tasks were planned in the "Programme..." [4]:

1. Conducting information and promotional activities about harmfulness of asbestos, safe handling of asbestos containing products and methods of their disposal,
2. Providing trainings for state administration employees concerning the regulations and procedures mandatory when handling asbestos,
3. Creating the Reference Centre for Research and Assessment of Occupational Asbestos-Related Risk,
4. Creating a data base concerning the location, amount and current state of asbestos containing products, predicted for disposal as dangerous wastes in communes, districts, provinces and the whole country and creating a data base necessary for efficient monitoring of the realization of tasks planned in the "Programme...", and training the employees of state administration to use these bases,
5. Developing plans of protection against asbestos harmfulness in communes, districts and provinces, as well as programmes of asbestos containing product disposal,
6. Supporting initiatives of local governments concerning cleaning public places of asbestos in order to:
   – complete cleaning of terrains and public facilities in communes especially contaminated with asbestos, once the hazard has been confirmed by the environmental tests and environmental risk assessment,
   – successive removal of dangerous products and their harmful effects for the inhabitants and the environment,
   – testing the air, soil and water in contaminated public places,
7. Construction of landfill for asbestos containing products,
8. Monitoring of the "Programme..." implementation.

Sources of financing the "Programme...". It was estimated that the expenditure on the programme realization in 2003–2032 will reach 48 238 million zlotys, in which:

– 47 198 million zlotys from private funds,
– 821.150 million zlotys from public funds,
– 212.850 million zlotys from foreign funds.

Supreme Chamber of Control (NIK) on disposal of asbestos and asbestos containing products in 2003–2005

In result of the inspection carried out, the Supreme Chamber of Control negatively evaluated the mode and way of realization of tasks connected with asbestos elimination from the territory of Poland in 2003–2005, as stated in the "Programme...". The analysis of the presented report shows that not all tasks involving development of communal, district and provincial programmes of asbestos and asbestos containing products removal were realized and the works connected with removing asbestos and asbestos containing products were not much advanced. Moreover, the Minister of Economy supervised the "Programme" coordinator only to a limited extent, cooperation between state and local government administration was unsatisfactory, which did not aid efficient realization of the programme objectives. The inspection revealed that from among the planned tasks only trainings on regulations and procedures of asbestos handling were organized. Out of the 1350 thousand zlotys allocated to this purpose for 2003–2032, the amount of 1087 thousand zlotys was spent by the end of 2005, which constitutes 81 % of the planned budget. The inspection demonstrated that out of the sum quoted above, 58.8 thousand zlotys was spend on training persons who were not public administration employees, which was an ineligible expenditure. The results of objective control point to unsatisfactory implementation of the other tasks, among others including development of actual situational plan of asbestos containing products in the area of provinces, preparation of full lists of objects containing asbestos and regions of asbestos hazard. The control showed also the lack of programmes for asbestos and asbestos containing products disposal, which should have been prepared for provinces, districts and communes. The inspection demonstrated that the main coordinator endeavoured to collect data about the amount and distribution of asbestos containing products by means of surveys. This activity did not produce expected results, since the surveys did not contain full data. It was established that since the programme was not updated systematically, it lacked details and therefore no new tasks were appointed, which in consequence did not establish the actual amount of asbestos and asbestos containing products on the territory of Poland. The reports prepared by the general coordinator and submitted to the Minister of Economy contained only information on trainings on legislation and procedures concerning asbestos and promotional activities, as well as the statement of expenditure on this purpose. The reports lacked information on the implementation of individual tasks planned in the programme in 2003–2005. The Supreme Chamber of Control stated that the programme was implemented unsatisfactorily with respect to cleaning the territory of Poland of asbestos [10, 12]. The rate at which asbestos containing products have been eliminated is too slow, whereas the local administration, particularly in communes is only negligently involved in these activities. The Programme developed in 2002 needs updating of terms and tasks, also because of Poland's integration with the European Union. Legal regulations concerning handling asbestos, currently in force, are primarily based on executive acts, which makes impossible execution of duties assigned to legal and physical entities. Continuation of the hitherto existing system of asbestos removal may make impossible realization of the programme objective, ie asbestos elimination from the territory of Poland by 2032. The report published by the Supreme Chamber of Control considered necessary undertaking by the Minister of Economy endeavours necessary for the development of updated version of the act banning the use of asbestos containing products or preparation of a different act on the problem of asbestos including the rights and duties of the appropriate public administration bodies, legal and physical entities [10, 12].

Conclusion

The most important remarks published in the "Report on programme realization in 2003–2007" will make up the conclusion of this paper:

– unsatisfactory number of programmes for asbestos and asbestos containing products elimination has been developed on the commune, district and province levels whereas works aiming at eliminating asbestos and asbestos containing products are too little advanced,

– there is an insufficient number of situational plans of asbestos containing products distribution in provinces or full lists of asbestos containing objects and regions threatened with asbestos effect,

– data on estimated number of sites where asbestos of asbestos containing products may be present has been verified unsatisfactorily,

– inventories of asbestos containing products and assessments of technical state of constructions in which asbestos or asbestos containing products are used are highly inadequate. Physical and legal entities prepared only about 110 thousand of building assessments during the period from 30 September 2004 to 31 December 2005, which made up only 7.3 % of the number of constructions containing asbestos products. This is the reason why there is no reliable information about the actual amount of asbestos, sites where it is present or the technical state of asbestos containing products in use.

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PRAWNO-ORGANIZACYJNE PROBLEMY REALIZACJI „PROGRAMU USUWANIA AZBESTU I WYROBÓW ZAWIERAJĄCYCH AZBEST NA TERYTORIUM POLSKI”

[1] Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie
[2] Instytut Administracyjno-Ekonomiczny
Państwowa Wyższa Szkoła Zawodowa w Tarnowie

Abstrakt: W pracy, po krótkim wprowadzeniu dotyczącym występowania, zastosowania oraz szkodliwości azbestu, przedstawiono podstawowe regulacje prawne w zakresie użytkowania i usuwania wyrobów zawierających azbest. Omówiono główne założenia „Programu usuwania azbestu i wyrobów zawierających azbest stosowanych na terytorium Polski”. Ocenę realizacji Programu przedstawiono na podstawie raportów kontrolnych Ministerstwa Gospodarki oraz NIK.

Słowa kluczowe: azbest, zagrożenia zdrowotne, regulacje prawne

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Iwona ADAMSKA[1*], Beata CZERNIAWSKA[1]
and Magdalena DZIĘGIELEWSKA[1]

MICROSCOPIC FUNGI OF THE LITTORAL ZONE IN SELECTED WATER BODIES OF THE POJEZIERZE BOBOLICKIE LAKELAND AND THE RÓWNINA GRYFICKA PLAIN

GRZYBY MIKROSKOPIJNE LITORALU WYBRANYCH ZBIORNIKÓW WODNYCH POJEZIERZA BOBOLICKIEGO I RÓWNINY GRYFICKIEJ

Abstract: The occurrence of parasitic fungi colonising the vegetation in the littoral zone of selected water bodies (two intrafield ponds, a class I lake and a class III lake) was studied in the period between 2006 and 2008. The study area comprised the Pojezierze Bobolickie lakeland and the Rownina Gryficka plain. A total of 64 plant species partly immersed in water or overgrowing the land were examined. The material was colonised by 90 species of fungi and fungi-like organisms. Anamorphic fungi predominated. The greatest number of fungi was represented by fungi of the genera *Septoria* and *Phyllosticta*. Only five species (*Cladosporium* sp., *Leptosphaeria caricis, Puccinia caricina, P. dioicae* and *Sphaerellopsis filum*) occurred in the littoral zones of all the water bodies. The majority of fungi observed in the study (63 % of species) were common in Europe while 33 species were identified as rare. Fungal species recorded in the study did not pose a pathogenic threat to crop plants. Diversified numbers of species found in individual water bodies resulted from the diversified species composition of the vegetation. Agrotechnical and chemical treatment conducted in adjacent fields and directly in the littoral zone of the water bodies considerably influence the species composition of fungi of intrafield ponds.

Keywords: fungi, parasitic fungi, *Ascochyta*, *Coniothyrium*, *Kuehneola*, *Leptosphaeria*, *Paraphaeosphaeria*, *Phaeosphaeria*, *Phyllosticta*, *Puccinia*, *Sphaerellopsis*, *Septoria*, *Stagonospora*, *Carex*, *Juncus*, Bobolice, Gościno, lake intrafield, intrafield pond, oligotrophic

The biological classification system of lakes is based on water productivity and distinguishes oligotrophic, mesotrophic and eutrophic lakes depending on nutrient richness and oxygen content. Oligotrophic reservoirs are low in mineral content and in organic substances in bottom sediments, and have well-oxygenated waters [1]. Water

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[1] Department of Plant Protection, West Pomeranian University of Technology, ul. J. Słowackiego, 71–434 Szczecin, Poland, phone 91 449 63 72.

* Corresponding author email: Iwona.Adamska@zut.edu.pl

bodies in Pomerania are mostly of this type [2]. Several protected species (eg *Lobelia dortmanna* and *Isoetes lacustris*) occur in the littoral zone of such lakes while plants typical of eutrophic water bodies (eg *Acorus calamus*, *Phragmites australis*, *Typha angustifolia* or *T. latifolia* [3]) are not observed in them.

The composition of intrafield ponds depends on the condition of groundwaters in the drainage basin. Such ponds are often polluted with heavy metals [4–8], undergo devastation or backfilling and disappear following drainage. This leads to disturbances in the ecological balance of adjacent areas [9–13]. The species composition of the vegetation surrounding intrafield ponds varies while the number of species depends on the width of the zone around the pond [14, 15]. However, all communities occurring in such areas are characterised by a small surface and zonality of occurrence [15].

Habitat conditions favourable for the formation and dispersal of fungal spores are recorded near lakes and ponds. Water bodies are usually formed in terrain depressions; air humidity is increased there and plant density is high. However, plants of intrafield ponds are susceptible to pesticides, including fungicides and herbicides, used for cereal crops. This considerably influences the composition of plants and fungi in such habitats. Oligotrophic lakes, on the other hand, occur in areas outside agricultural production, often in forests, where plants and fungi are not similarly affected by anthropopressure.

The aim of the study was to determine the number of fungal species colonising the vegetation of intrafield ponds and class I and class III lakes and to compare the taxonomic structure of the organisms identified in the study.

Material and methods

Investigations were conducted in the vicinity of the villages of Porost (Pojezierze Bobolickie lakeland) and Goscino (Rownina Gryficka plain) from 2006 until 2008. An oligotrophic lake (lake Jezioro Piekielko near Porost), a class III lake (lake Jezioro Kamienica near Goscino) and two intrafield ponds connected by a small watercourse (situated near Porost) were selected for analysis. Leaves and stems of plants with pathological changes (leaf spots, chlorosis, wilting, outgrowths, oozing) and aetiological changes (an evident layer of mycelium and fungal sporulation) were used as the study material. The vegetation both partly immersed in water and overgrowing the land (up to 10 m from the lake shore) was examined.

Plant fragments were collected, transported to the laboratory, conserved and analysed. Small fragments of pathological tissues were cut out with a safety razor and cut into small strips. They were placed in a drop of lactic acid on a microscopic slide and covered with a cover slip. A microscopic analysis was conducted two days after slide preparation. Parasitic and saprotrophic fungi were identified using the size, structure and colour of the fruitbodies and spores.

Keys and guides [16–19] were used to determine the species. Fungi were identified and their occurrence was defined based on studies and monographs [20–25]. The systematics of fungi was accepted after Hawksworth et al [26] and only the previous division into the orders *Moniliales*, *Melanconiales* and *Sphaeropsidales* was retained for anamorphic fungi. The nomenclature of fungi was standardised and given after

Mulenko et al [25]. The plant material was deposited as a herbarium at the Departament of Plant Protection, West Pomeranian University of Technology, Szczecin.

Only lists of fungi and brief descriptions of them are provided in previous publications reporting preliminary results of studies into fungi colonising selected intrafield ponds and lakes [27–29].

Results and discussion

The study material consisted of 64 plant species. Of them, 27 species were collected around the intrafield ponds, 33 species were collected in the littoral zone of lake Jezioro Piekielko and 20 species were collected in the littoral zone of lake Jezioro Kamienica. Species of the families *Cyperaceae* and *Poaceae* dominated among hosts, and *Carex* was the most frequently examined genus. Two species of fungi also served as hosts.

The study material was colonised by a total of 90 species of fungi and fungi-like organisms (FLO). Anamorphic species dominated among the taxa (63 species; 70 % of fungi) while representatives of *Oomycota* were the smallest group (4 species; 4.4 %). The greatest number of fungi identified in the study represented the order *Sphaeropsidales* (42 species; Table 1) and the smallest number represented the orders *Pythiales* and *Leotiales* (one taxon each).

Table 1

The species structure of fungi at individual study sites

Fungi	Lake Jezioro Kamienica	Lake Jezioro Piekielko	Intrafield ponds	Total
Peronosporales	2	1	—	3
Pythiales	1	—	—	1
Erysiphales	—	1	2	3
Leotiales	—	—	1	1
Pleosporales	3	8	3	9
Uredinales	4	5	7	10
Moniliales	3	8	5	15
Melanconiales	1	4	1	6
Sphaeropsidales	11	19	19	42

The fungi belonged to 41 genera. The greatest number of genera (28) represented anamorphic fungi while the smallest (3) – *Oomycota* and *Basidiomycota*. The genera *Septoria* and *Phyllosticta* were represented by the greatest number of species (12 taxa each).

Only two taxa were classified as polyfagous saprotrophs (*Alternaria alternata* and *Cladosporium* sp.). They colonised hosts belonging to different plant families in the study area. One taxon (*Sphaerellopsis filum*) was a hyperparasite commonly recorded in Poland [30, 31]. It colonised aecia of rusts and caused the destruction of aeciospores.

The vegetation overgrowing the ponds shores was colonised by 38 fungal species. Twenty four taxa were colleted in the vicinity of lake Jazioro Kamienica and 46 taxa near lake Jezioro Piekielko.

Anamorphic fungi dominated in the littoral zone of the water bodies (Fig. 1). They constituted between 57 % of organisms recorded near lake Jezioro Kamienica and 67 % near lake Jezioro Piekielko. Fungi of the phylum *Ascomycota* had a higher percentage occurrence near lake Jezioro Piekielko (20 %) and a lower percentage occurrence near lake Jezioro Kamienica (13 %). The highest share of *Basidiomycota* was recorded near the intrafield ponds (18 %) and the smallest near lake Jezioro Piekielko (11 %). Fungi-like organisms of the phylum *Oomycota* occurred only in the littoral zone of lakes Kamienica and Piekielko, and were 13 % and 2 % of fungi indentified in the study, respectively.

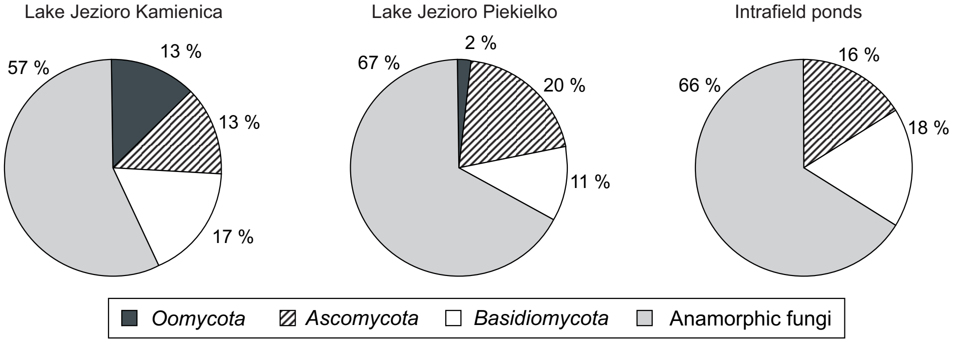

Fig. 1. The taxonomic structure of species of fungi and FLO recorded in the littoral zone of the lakes

Fungi of the order *Sphaeropsidales* predominated in the water bodies (Table 1). The smallest number of species (one taxon each) represented the orders *Melanconiales* and *Pythiales* in lake Jezioro Kamienica, the orders *Peronosporales* and *Erysiphales* in lake Jezioro Piekielko, and the orders *Leotiales* and *Melanconiales* in the intrafield ponds.

Cladosporium sp., *Leptosphaeria caricis*, *Puccinia caricina*, *P. dioicae* and *Sphaerellopsis filum* were fungal species collected in the littoral zone of all the water bodies. *L. caricis*, *P. caricina* and *P. dioicae* colonised leaves of many species of the genus *Carex* causing their frequent occurrence at the study sites. *S. filum* parasitized in aecia of *P. dioicae* and *P. caricina*.

Fungi of the genus *Septoria* (7 species) were the most numerous group of fungi recorded near lake Jezioro Piekielko although the genus *Stagonospora* (6 species) also had a relatively high number of representatives. Representatives of the genus *Puccinia* (4 species) predominated near lake Jezioro Kamienica and of the genus *Phyllosticta* near the intrafied ponds (7 species).

The occurrence frequency of fungi identified in the study in Poland was determined using *A preliminary checklist of micromycetes in Poland* [25]. The analysis showed that the majority of fungi recorded in the plant material (57 species; 63 % of the taxa) commonly occur in Poland. Thirty three species were classified as rarer taxa (recorded at 1–3 sites in Poland), including *Ascochyta tussilaginis* (An*), *Coniothyrium psammae* (An), *Hendersonia culmiseda* (An), *Kuehneola uredinis* (B), *Leptosphaeria juncina* (A), *Massarina arundinacea* (A), *Paraphaeosphaeria michotii* (A), *Phaeosphaeria caricis* (A), *P. nigrans* (A), *Phyllosticta caricina* (An), *Septoria bresadoleana* (An), *S. rumicis* (An), *Stagonospora caricinella* (An) and *St. innumerosa* (An; *symbols: A – *Ascomycota*, B – *Basidiomycota*, An – anamorphic fungi). The majority of taxa rarer in Poland were recorded on plants of the genus *Carex*.

The occurrence frequency of the majority of fungi in the study material was high. Representatives of the genera *Puccinia* and *Stagonospora* were the most widespread organisms. Fungi colonising wild-living plants or their ornamental varieties only were the largest group; they did not pose a pathogenic threat to crop plants.

Fungi colonising the water bodies were characterised by a high biodiversity. The number of their taxa was always higher than that of hosts colonised by them. The taxonomic structure of fungi in the water bodies was typical of natural areas (low anthropopressure) as anamorphs predominated [11]. However, the vegetation of the intrafield ponds was colonised by a smaller number of parasitic and saprotrophic fungi than that in the littoral zone of the oligotrophic lake (Jezioro Piekielko) and higher than that in the class III lake (Jezioro Kamienica). The number of plant species forming the littoral zone most probably had the determining influence on the species composition of fungi in the reservoirs. Protective treatment conducted during agricultural production in fields adjacent to the pond or the destruction of dried plants (burning) in the spring may also have been an important factor in the case of the intrafield ponds.

Parasitic fungi colonising plants of the littoral zone were also examined in Western Pomerania [32, 33] and the Masurian Lakeland [34–36]. Anamorphic fungi always predominated at the study sites. Species of plant parasites commonly occurring in the study area were mostly recorded [36]. The greatest number of fungi near water bodies colonised plants of the genera *Phragmites* and *Carex* [33]. Water plants of the genera *Elodea*, *Lemna*, *Nuphar* and *Potamogeton* showed the greatest resistance to fungal pathogens [36]. However, the floristic diversity of an association was not always positively correlated with the diversity of fungi colonising individual plants of the association [33]. According to Durska [35, 36], the number of biogens in the habitat influenced the biodiversity of fungi of the littoral zone. A higher number of species was recorded at sites with the substrate richer in organic content than in poor habitats. Obligatory parasites developed better on abundant and well-nourished plants while facultative parasites preferred weakened hosts [36]. Mazurkiewicz-Zapałowicz et al [33] also found a relationship between the occurrence of fungi and habitat conditions at the site, and especially the local climate and the location of the study site. Mazurkiewicz-Zapałowicz et al showed that open and airy sites were more favourable for the migration of spores than sites located in terrain depressions. The amount of light reaching the site was also important as strong insolation encouraged a more numerous occurrence of rusts and faster sporulation [36]. The structure of the host plant and the growth type also influenced the occurrence of fungi. A greater diversity of fungi was recorded on taller plants and on plants forming large clumps [33]; distinct preferences of fungi for individual plant fragments were also shown (a different species composition of fungi was recorded on culms, stems and leaves of one plant [32]).

Conclusions

1. The number of fungal species colonising the vegetation of two intrafield ponds was lower than that of species recorded in the littoral zone of a class I lake and higher than that on plants of a class III water body.
2. The diversified composition of the vegetation overgrowing the shores resulted in a diversified number of fungi in individual water bodies.
3. The analysis of the taxonomic structure of fungi showed that anamorphic fungi predominated. This is typical of plants in natural communities.
4. Fungi colonising the vegetation of the littoral zone of the lakes and intrafield ponds did not pose a pathogenic threat to crop plants.
5. The lower biodiversity of fungi observed in the littoral zone of the intrafield ponds than in the oligotrophic lake was associated with chemical treatment conducted in cultivated fields and with the burning of plant remains.

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GRZYBY MIKROSKOPIJNE LITORALU WYBRANYCH ZBIORNIKÓW WODNYCH POJEZIERZA BOBOLICKIEGO I RÓWNINY GRYFICKIEJ

Zakład Ochrony Roślin
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

Abstrakt: W latach 2006–2008 przeprowadzono badania nad występowaniem grzybów pasożytniczych zasiedlających roślinność litoralu wybranych zbiorników wodnych (oczka śródpolnego oraz jezior o wodach I i III klasy czystości). Teren badań obejmował Pojezierze Bobolickie i Równinę Gryficką. Badaniom poddano 64 gatunki roślin częściowo zanurzone w wodzie lub porastające ląd. Analizowany materiał zasiedlało 90 gatunków grzybów i FLO. Wśród nich dominowały grzyby anamorficzne. Największa liczba gatunków reprezentowała grzyby z rodzajów *Septoria* i *Phyllosticta*. Tylko pięć gatunków (*Cladosporium* sp., *Leptosphaeria caricis, Puccinia caricina, P. dioicae* i *Sphaerellopsis filum*) występowało równocześnie w litoralach wszystkich badanych zbiorników. Większość znalezionych grzybów (63 % gatunków) było pospolitych dla Europy, a 33 uznano za rzadkie. Rozpoznane gatunki grzybów nie stanowiły zagrożenia chorobowego dla roślin uprawnych. Powodem zróżnicowanej liczby gatunków znajdywanych w poszczególnych zbiornikach był zróżnicowany skład gatunkowy roślinności. Na skład gatunkowy grzybów oczek śródpolnych duży wpływ mają zabiegi agrotechniczne i chemiczne prowadzone na przyległych polach oraz bezpośrednio w obrębie litoralu zbiornika.

Słowa kluczowe: grzyby, grzyby pasożytnicze, *Ascochyta*, *Coniothyrium*, *Kuehneola*, *Leptosphaeria*, *Paraphaeosphaeria*, *Phaeosphaeria*, *Phyllosticta*, *Puccinia*, *Sphaerellopsis*, *Septoria*, *Stagonospora*, *Carex*, *Juncus*, Bobolice, Gościno, jezioro śródpolne, oczko śródpolne, oligotroficzne

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Agnieszka BĘŚ[1]

CARBON DIOXIDE EMISSIONS FROM FLY-ASH IN THE RECLAMATION PROCESS

EMISJA DITLENKU WĘGLA Z POPIOŁÓW LOTNYCH W PROCESIE REKULTYWACJI

Abstract: The objective of this study was to determine the amount of carbon dioxide emitted from fly-ash reclaimed by sewage sludge and municipal waste compost, measured at a temperature of 10, 20 and 30 °C and a substrate moisture content of 60 % of maximum water capacity. Samples of ash and sludge substrates and ash and compost substrates were collected at the end of the growing season. The following mixtures were used in the study: ash with a 25 % and 50 % sludge or compost addition. Carbon dioxide emission was determined by the absorption method with the use of 0.05 mol NaOH · dm^{-3}. Substrate samples were put in 1 litre jars and placed in a controlled environment chamber (Microclima 1000, Snijder Scientific B.V.). Samples were incubated for 72 hours. The obtained results were verified by the ANOVA analysis of variance (F test) for multi-factorial designs.

The results of the study indicate that compost and sewage sludge increase the respiratory activity of fly-ash. The rate of carbon dioxide evolution was affected by incubation temperature – a more than a 300 % increase in CO_2 emission was reported when incubation temperature was raised from 10 °C to 30 °C.

Keywords: carbon dioxide, emission, fly-ash, reclamation

Fly-ash from the process of coal combustion for energy production constitutes highly noxious waste. In Poland, this type of waste is neutralised mostly by disposal in repositories. Fly-ash can be utilised in road and industrial construction, in the production of construction and ceramic materials, it is also deployed to stabilise soils, to fill excavation pits, reclaim degraded areas and treat municipal waste [1–4]. Combustion waste deposited at landfill sites is a source of dust pollution and it requires reclamation. One of the methods of reclaiming energy waste sites involves the introduction of organic substances followed by sodding [5].

Carbon dioxide emissions are determined, among others, by the rate of fossil fuel exploitation, biomass combustion and industrial activity. Deforestation is a major

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[1] Department of Air Protection and Environmental Toxicology, University of Warmia and Mazury in Olsztyn, pl. Łódzki 2, 10–726 Olsztyn, Poland, phone +48 89 523 3336, fax +48 89 523 3381, email: agnieszka.bes@uwm.edu.pl

contributor to higher CO_2 emissions. Carbon dioxide is also formed during the respiratory activity of various organisms, and it is absorbed by plants in the process of photosynthesis. The rate of CO_2 formation in soil is affected by the following factors: temperature, moisture content, pH level of soil and the type of soil use [6, 7].

The intensity of carbon dioxide emissions may be an indicator of biological processes taking place in the soil. This study attempts to determine the amount of carbon dioxide emitted by fly-ash from coal combustion, reclaimed with the use of sewage sludge and compost. The study was carried out under controlled temperature and humidity conditions on the assumption that temperature and moisture content are the main determinants of CO_2 emission.

Materials and methods

The study was performed with the use of material from a 6-year pot experiment which aimed to determine the influence of sewage sludge and compost on fly-ash reclamation. Fly-ash was mixed with sewage sludge and compost at different proportions. The experimental treatments are presented in Table 1. The experiment was carried out in three replicates.

Respiratory activity, measured in terms of carbon dioxide emission, was investigated in the sixth year of the experiment at the end of the growing season.

Fly-ash used in the experiment was obtained from the Municipal Heating Plant (MPEC) in Olsztyn. In line with soil classification standards, the investigated ash was classified as sandy silt. In the first year of the experiment, the carbon content of ash was determined at 12.86 % at a pH level of 8.8. The compost used in the experiment consisted of stabilised sewage sludge, leaves, grass, sawdust and organic wastes. The carbon content of compost was 5.3 % with pH of 7.7 in 1 mol KCl $\cdot$ dm^{-3}. Sewage sludge with a muddy consistency was obtained from the sludge-drying beds of the Municipal Waste Treatment Plant in Olsztyn. Sludge was abundant in nutrients: its organic carbon content reached 7.48 % with water pH of 7.9. Fresh sewage sludge with a 54.32 % dry matter content was used in the experiment.

Carbon dioxide emissions were determined by the absorption method with the use of 0.05 mol NaOH $\cdot$ dm^{-3}. Pot samples were brought to a moisture content of 50 % of maximum water capacity. They were placed in a controlled environment chamber (Microclima 1000, Snijder Scientific B.V.) in tight, 1 litre jars. Carbon dioxide emission was measured at three temperature settings: 10, 20 and 30 ^{o}C. The amount of emitted carbon dioxide was determined as described by Isermeyer [8]. The analysed substrates were brought to the desired moisture content and incubated in a phytotron chamber at the set temperature for 72 hours. Carbon dioxide emissions were measured every 24 hours, when the jars were aired and filled with fresh NaOH solutions. The applied methodology has been described in detail by Rogalski and Bes [9].

The obtained results were verified by the ANOVA analysis of variance (F test) for multi-factorial designs. Two experimental factors were adopted: dose of sewage sludge or compost and incubation temperature. Significant differences were determined by the Newman-Keuls test at a significance level of p = 0.01. The results of post-hoc tests are presented as homogenous groups and are denoted by respective letters in the results tables. The relationships between the tested parameters were determined with the use of Pearson linear correlation between two variables. The significance of correlation coefficients *r* was estimated at a significance level of $p < 0.01$. Statistical analyses were performed with the use of STATISTICA 8.0 PL software (StatSoft Inc. 2007).

The term *substrate* used in this study refers to both fly-ash as well as mixtures of fly-ash with sewage sludge and compost.

Results and discussion

The results of the study indicate that both the sludge and compost dose and the incubation temperature had a statistically significant impact on carbon dioxide emissions. The interactions between the investigated factors also significantly influenced the analysed parameter.

The mean emission values for all experimental treatments are presented in Table 1.

Table 1

Carbon dioxide emission [$mg \cdot kg^{-1}$ d.m. substrate $\cdot d^{-1}$] on individual experimental treatments

Treatment	Temperature [^oC]			Mean for treatment
	10	20	30	
Fly-ash	38.62 a	91.45 cde	111.13 de	80.40 A
Sewage sludge	83.82 bcde	72.80 bc	156.94 f	104.52 B
Compost	24.25 a	241.54 h	204.90 g	156.90 D
Fly-ash + sewage sludge (75 % + 25 %)	93.62 cde	113.26 e	208.87 g	138.58 C
Fly-ash + sewage sludge (50 % + 50 %)	50.23 ab	102.03 cde	108.79 cde	87.02 AB
Fly-ash + compost (75 % + 25 %)	76.11 bcde	208.91 g	368.43 i	217.82 E
Fly-ash + kompost (50 % + 50 %)	37.74 a	73.97 bcd	181.62 fg	97.78 AB
Mean for temperature	57.77 x	129.14 y	191.53 z	

Values denoted by different letters are significantly different at $p = 0.01$; values are denoted by letters: a, b, ... for a comparison of dependencies between substrate type and temperature; A, B, ... for a comparison of substrate types; x, y, z – to determine the impact of temperature on carbon dioxide emission; these values belong to different homogenous groups (based on post-hoc tests).

Impact of sludge and compost dose on CO_2 emission

The addition of sewage sludge and compost to fly-ash resulted in higher CO_2 emissions from the analysed substrates in comparison with the control treatment which comprised fly-ash only. The noted differences between CO_2 emissions from substrates with a 25 % and 50 % sludge or compost content were statistically significant.

CO_2 emission was higher in treatments where fly-ash was mixed with 25 % sludge – the share of those emissions for all temperature settings increased by 72 % on average. In treatments with a 50 % sludge content, CO_2 emissions rose only by 8 % (in comparison with control). Similar dependencies were reported in treatments with a fly-ash and compost mixture – the addition of compost in the amount of 25 % and 50 % increased CO_2 emissions by 170 % and 22 %, respectively. The studies carried out by Nosalewicz [7], Quemada and Menacho [10], Gostkowska et al [11], Wong and Lai [12] to determine the amount of CO_2 emitted from different substrates fertilised with mineral and organic substances show that the addition of fertilisers increased CO_2 emissions. The above trend is supported by the results of this experiment. It should be noted, however, that a 25 % compost or sludge addition led to a much higher increase in CO_2 emissions than a 50 % dose. In a study investigating CO_2 emissions from soils transformed as a result of gravel excavation, Rogalski et al [13] observed that fly-ash mixtures with a 50 % sludge content increased carbon dioxide emissions by 39 %. CO_2 emissions from treatments supplied with 25 % sludge rose by only 13 %. A similar dependency to that noted in this study was reported by Rogalski and Bes [9] in their analysis of fly-ash and sludge substrates in the second year of the experiment conducted before the growing season.

Impact of temperature on CO_2 emissions

A statistical analysis pointed to significant differences in CO_2 emissions for every temperature range. In view of the mean levels of CO_2 emission reported in all experimental treatments, when the samples were incubated at 10 ^{o}C, carbon dioxide emissions reached 57.77 $mg \cdot kg^{-1} \cdot d^{-1}$. A 10 ^{o}C rise in incubation temperature (from 10 ^{o}C to 20 ^{o}C) increased CO_2 emissions by 123 %. When the temperature was increased by another 10 ^{o}C (from 20 ^{o}C to 30 ^{o}C), emissions rose by 48 %. The greatest change in the amount of emitted CO_2 was noted when incubation temperature was increased from 10 ^{o}C to 20 ^{o}C. As regards the fly-ash and compost mixture (75 % + + 25 %), a 10 ^{o}C increase in incubation temperature raised carbon dioxide emissions by 175 % (from 76.11 to 208.91 $mg \cdot kg^{-1} \cdot d^{-1}$). In the remaining treatments, CO_2 emissions increased from 21 % to 137 %. When incubation temperature was raised by another 10 ^{o}C, the emission levels of the analysed gas increased by 7 % to 146 %. Carbon dioxide emissions increased by 231.5 % on average when incubation temperature rose by 20 ^{o}C (from 10 ^{o}C to 30 ^{o}C). In a study conducted by Rogalski et al [13], the respiratory activity of light soil fertilised with sewage sludge increased proportionally to the rise in incubation temperature. Carbon dioxide emissions from substrates incubated at 30 ^{o}C were 466 % higher than from the same substrates incubated at 10 ^{o}C. The optimal incubation temperature for the substrates analysed in this study was 20 ^{o}C and it is consistent with the findings of, among others, Wlodarczyk et al [14] and O'Connel [15].

The analysis of Pearson linear correlation between two variables showed that carbon dioxide emissions were not correlated with the applied compost or sludge dose. Statistically significant correlations were observed between incubation temperature and CO_2 emissions at $r = 0.72$ ($p < 0.01$, $n = 27$) for fly-ash and sludge substrates, and at $r = 0.69$ ($p < 0.01$, $n = 27$) for fly-ash and compost substrates.

Conclusions

1. The results of this experiment suggest that the addition of fly-ash to sewage sludge and municipal waste compost contributes to an increase in CO_2 emissions. Carbon dioxide emissions from fly-ash and compost substrates were on average by 40 % higher than from fly-ash and sludge mixtures.

2. The addition of sewage sludge or compost to fly-ash led to statistically significant differences in the amount of emitted CO_2. The obtained results indicate that a content of organic substances in substrates increased CO_2 emissions by 68 % on average.

3. The amount of emitted CO_2 was significantly affected by incubation temperature. A temperature rise of 10 ^{o}C increased emission levels by 86 % on average in all treatments. The optimal temperature for the analysed substrates was 20 ^{o}C.

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EMISJA DITLENKU WĘGLA Z POPIOŁÓW LOTNYCH W PROCESIE REKULTYWACJI

Katedra Ochrony Powietrza i Toksykologii Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Celem pracy było określenie ilości wydzielonego ditlenku węgla z popiołu lotnego rekultywowanego osadem ściekowym oraz kompostem z odpadów komunalnych, w ustalonych temperaturach: 10, 20 i 30 ^{o}C, przy wilgotności podłoży równej 60 % maksymalnej pojemności wodnej. Próbki podłoży popiołowo-osadowych i popiołowo-kompostowych pobrano po zakończeniu okresu wegetacji. W doświadczeniu wykorzystano następujące mieszaniny: popiół z 25 % i 50 % dodatkiem osadu lub kompostu. Pomiar emisji ditlenku węgla prowadzono metodą absorpcyjną z 0,05 mol NaOH $\cdot$ dm^{-3}. Słoje o pojemności 1 litra, z próbkami odpowiednich podłoży, umieszczano w komorze klimatyzacyjnej Microclima 1000 (Snijder Scientific B.V.). Próbki inkubowano przez 3 doby. Wyniki uzyskane z badań poddano analizie wariancji ANOVA (test F) dla układów wieloczynnikowych.

Przeprowadzone badania wykazały, że dodatek kompostu lub osadu ściekowego powoduje zwiększenie aktywności respiracyjnej popiołu lotnego. Intensywność wydzielania ditlenku węgla zależała od temperatury inkubacji i przy jej wzroście z 10 ^{o}C do 30 ^{o}C emisja CO_2 zwiększyła się o ponad 300 %.

Słowa kluczowe: ditlenek węgla, emisja, popiół lotny, rekultywacja

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Jacek CZEKAŁA[1]

CHANGES OF CADMIUM, NICKEL AND LEAD CHEMICAL BONDS IN A SEWAGE SLUDGE-BASED COMPOST

ZMIANY CHEMICZNYCH POŁĄCZEŃ KADMU, NIKLU I OŁOWIU W KOMPOŚCIE WYTWORZONYM NA BAZIE OSADU ŚCIEKOWEGO

Abstract: The aim of the performed investigations was to determine changes which take place in chemical bonds of cadmium, nickel and lead fractions during sludge composting with the addition of sawdust and straw under conditions of an outdoor composting plant. For this purpose, a tractor compost-heat aerator was used which mixed, chopped and aerated the compost. Heap composting lasted 110 days and then the experimental composts were subjected to maturation (250 days). Samples for analyses were collected on day: 1, 54, 110 and 360 of the experiment using the BCR method (recommended by the Commission of the European Bureau Community of Reference) for metal sequential analysis.

It was found that quantitative changes as well as the proportion of individual metal fractions concerned, primarily, chemical bonds of soluble fractions, while metal bonds with silicate minerals (residual) were affected only slightly. In the discussed composting conditions, it was observed the highest increase in the proportion of the exchangeable and easily-soluble fractions of cadmium in the mature compost which should be considered as an unfavorable process. On the other hand, cadmium and lead decreased proportions of their chemical bonds with organic matter, while nickel increased them.

The residual fraction in the mature compost constituted 38.2 % (cadmium), 63.1 % (nickel) and 84.9 % (lead) of their total contents.

Keywords: compost, chemical bonds, cadmium, nickel, lead

Sewage sludges from communal sewage treatment plants pose increasingly serious social, economic and, first and foremost, ecological problems. According to data provided by the Main Statistical Office (GUS) [1], 501.3 Gg (thousand tons) dry matter of sludges were obtained from domestic communal sewage treatment plants of which 80.6 Gg, ie approximately 16.1 %, were utilized in agriculture. However, the dynamics of sludge production is exceptionally high and, according to various predictions, it may increase to over 706 Gg dry matter annually in a future [2, 3].

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[1] Department of Soil Science and Land Protection, Poznan University of Life Sciences, ul. Szydłowska 50, 60–656 Poznań, Poland, email: jczekala@up.poznan.pl

Bearing in mind the chemical composition of sludges [4–7], they constitute a serious source of organic matter and nutrients which should be returned to the soil in natural geochemical cycle. However, sludge contain also mineral and organic contaminations in their composition [8, 9] which restrict their utilization in their crude, untreated form.

Therefore, composting appears to be one of possible, biologically acceptable ways of sludge utilization during which, although it is impossible to eliminate trace elements, it is nevertheless possible to transform them into forms less available to plants.

The paper presents results of investigations concerning cadmium, nickel and lead chemical fractions in composts manufactured from sewage sludge, straw and sawdust.

Material and methods

The experimental material derived from the authors own experiments on the composting of sewage sludge carried out in an outdoor composting plant in Czarnkow. The experimental compost was prepared from sewage sludge which constituted 70 % of the compost bulk (converted into dry matter), straw (20 %) and sawdust (10 %). The compost pile of 4130 Mg dry matter initial bulk was subjected to the composting process during the period of 110 days employing a tractor compost heap aerator. After this period, the heap was allowed to mature for the following 250 days. Compost samples for analyses were collected from the heap on days: 1, 54, 110 and 360 of the experiment. The collected samples were dried at the temperature of 40 ^{o}C, ground and subjected to analytical procedures. Selected compost properties are presented in Table 1.

Table 1

Selected properties of sewage sludge, straw, sawdust and composts

Parameter	Unit	Sewage sludge	Saw dust	Straw	Compost – Days of composting			
					1	54	110	360
OM[1]	[g · kg^{-1} d.m.]	645.2	764.0	940.0	763.0	764.0	749.0	667.0
C_{org}		435.7	456.3	435.2	340.3	299.6	284.3	358.0
Ash		354.8	236.0	60.0	237.0	236.0	251.0	333.0
Cd	[mg · kg^{-1} d.m.]	4.32	0.98	1.60	3.85	5.44	5.18	5.41
Ni		40.5	12.6	5.57	26.60	27.90	28.10	28.50
Pb		43.2	43.7	7.11	33.40	35.20	36.70	43.80

[1] Organic matter.

Total heavy metals were determined in *aqua regia*. Half gram of fairly-dried compost was digested with 5 cm^3 HNO_3 and 15 cm^3 HCl [10] in a reaction vessel [11]. After digestion, it was filtered into a 100 cm^3 volumetric flask and diluted to the mark with distilled water. Elements content were determined by the AAS methods.

Sequential analysis of the chemical bonds of the examined elements was carried out using the BCR method according to the procedure presented by Tokalioglu et al [12] and shown in Table 2.

Table 2

Sequential extraction scheme for cadmium, nickel and lead in compost

Step	Procedure	Compost fraction
I	32 cm^3 of 0.11 $mol \cdot dm^{-3}$ CH_3COOH per 0.8 g of d.m. compost samples were added and shaken at the temperature of 50 °C, pH 2.85	Exchangeable ions, water and acid soluble
II	32 cm^3 of hydroxylamine chloride ($HONH_2 \cdot HCl$) solution of 0.1 $mol \cdot dm^{-3}$ adjusted to pH 2 with HNO_3 was added to the solid residue and extracted for 16 h at 50 °C	Reducible; iron/manganese oxides
III	8 cm^3 H_2O_2 (9.8 $mol \cdot dm^{-3}$) was carefully added in residue samples and digested firstly for 1 h at 25 °C, and then for 1 h at 85 °C in a water bath with a second volume of H_2O_2. Next the solution was evaporated to near dryness. Hereafter, a 40 cm^3 of ammonium acetate (1 $mol \cdot dm^{-3}$) adjusted to pH 2 (with HNO_3), at temperature of 25 °C	Oxidizable species (organic substance and sulphides)

The above method is recommended for sequential analysis [13] and is used not only for sewage sludges but also for benthos deposits, soils and composts [10, 14–16].

Analyses of concentrations of the examined heavy metals were performed by atomic absorption spectrometry using a Varian Spectra plus model spectrometer with air/acetylene flame. The unextracted residues of elements were determined from the difference between the total content and the sum of three fractions.

Experimental data were statistically worked out on the basis of the one-factorial analysis of variance (ANOVA) by using the STATISTICA 8.0 software.

Results and discussion

Heavy metals constitute an integral constituent of sewage sludges including those obtained from communal sewage treatment plants. Their contents vary and are subject to strict legal regulations limiting their content when intended for agricultural or natural utilization [17]. However, it should be clearly emphasized that their total concentrations indicate only possible hazards to the environment and do not characterized them from the point of view of their availability for plants or mobility in the environment, for example soil.

It is evident from experiments [18] that individual trace elements occurring in sewage sludges may differ not only with regard to varying contents but also with regard to chemical bonds. According to the above researchers, cadmium occurred in sludges in all the examined chemical bonds, of which easily soluble forms constituted 9.2 % of the total content, although 28 % were non-soluble bonds.

Generally speaking, composted sludges are the main source of compost contamination with metals. In experimental conditions, the sludge contained, on average: cadmium – 4.32 $mg \cdot kg^{-1}$ d.m., nickel – 40.4 $mg \cdot kg^{-1}$ d.m. and lead – 43.2 $mg \cdot kg^{-1}$ d.m. Total contents of metals on the day of initiation of experiments decreased as a result of material dilution with organic matter but with the passage of time their quantities in composts increased (Table 1) which is a natural process connected with organic matter mineralization.

In the crude sludge, the easily soluble fraction (F I) – in which metals are defined as exchangeable, water-soluble and associated with carbonates – was found to be at a similar level for all three elements and constituted from 10.0 to 10.7 % of the total content (Fig. 1). The above values should be considered as high bearing in mind general positive dependence of metals in their available forms on their total contents [19, 20].

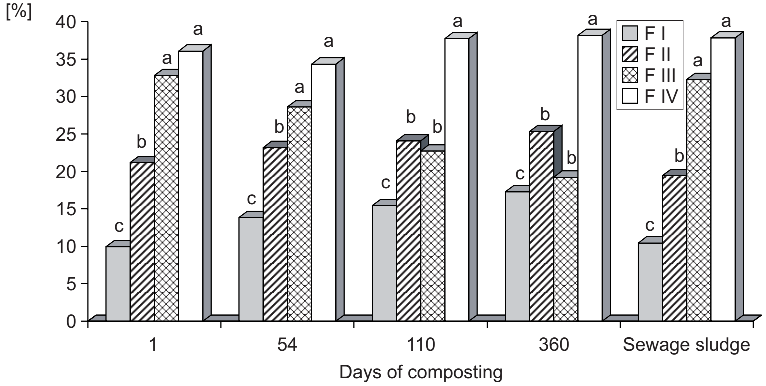

Fig. 1. Percentage of cadmium speciation in chemical fractions of compost (F I – Exchangeable, water soluble and carbonate bound; F II – Fe-Mn oxide bound; F III – Organic matter and sulphides bound; F IV – Residual)

Sludge composting caused significant differences in the proportion of chemical bonds of these metals. In the case of cadmium from the mature compost, a distinct increase of the content was determined in its exchangeable, ie easily available, fraction (17.27 %) against 9.93 % on the first day of investigations.

On the other hand, the proportion of nickel and lead decreased in comparison with the sludge alone as well as the compost on the day of the establishment of the experiment to 8.46 % (Fig. 2) and 5.00 % (Fig. 3), respectively. With regard

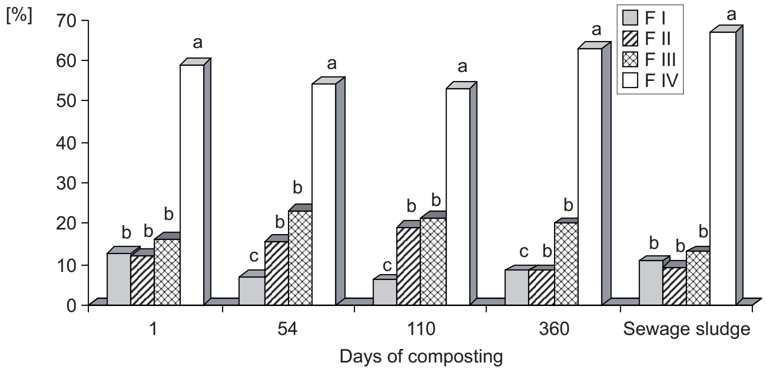

Fig. 2. Percentage of nickel speciation in chemical fractions of compost (F I – Exchangeable, water soluble and carbonate bound; F II – Fe-Mn oxide bound; F III – Organic matter and sulphides bound; F IV – Residual)

to cadmium, the observed changes in its proportion took place, primarily, at the expense of bonds with organic matter with which 32.83 % of the total quantity of cadmium was bonded at the initiation of the experiment and only 19.23 % in the mature compost. A similar tendency was observed in the case of lead (10.00 and 4.05 %, respectively).

On the other hand, with the passage of time nickel content increased its proportion in its bonds with organic matter from 16.15 % to 20.00 % in the mature compost. These are not high values but indicate unambiguously the direction of changes of this element during the process of sludge composting (Fig. 2). These results fail to corroborate the reports of Kazi et al [21] who determined the highest share of nickel in the fraction of sludge organic compounds but are in agreement with the reports [22] about the accumulation of this element mainly in the residual fraction.

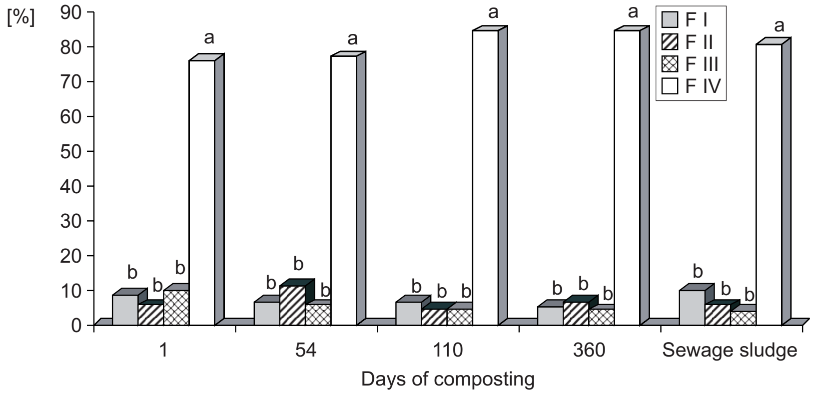

Fig. 3. Percentage of lead speciation in chemical fractions of compost (F I – Exchangeable, water soluble and carbonate bound; F II – Fe-Mn oxide bound; F III – Organic matter and sulphides bound; F IV – Residual)

It is worth emphasizing that during the composting of sewage sludges, transformations of chemical bonds of metals contained in them took place, primarily, in the first three fractions with only slight modifications of non-soluble bonds (F IV). Bonds of the residual fraction are associated strongly with silicate minerals as well as with other durable complexes and are considered chemically and biologically stable and inactive. Bearing in mind the observed decreasing mobility of metals in consecutive fractions (F I > F II > F III > F IV), it can be concluded that, from ecological point of view, sludge composting with sawdust and straw was found to favor most the increased cadmium solubility distinctly limiting the solubility of lead. However, lead appears to be an exceptional element due to its limited solubility of its inorganic compounds in the result of the development of poorly- or non-soluble bonds [23]. On the other hand, lead does not undergo biodegradation and decomposition which, to a certain degree, restricts its mobility in the soil. On the other hand, nickel by nature forms bonds, including complex ones, with humic compounds.

Conclusion

1. Chemical transformations of cadmium, nickel and lead bonds in the examined compost underwent changes in the course of the composting process, primarily, within easily-soluble and reduction fractions as well as within the fraction associated with organic matter.

2. Composting was found to increase only the proportion of cadmium in fractions characterized by very easy and easy metal mobility, while its connections with organic matter decreased.

3. Nickel was the only metal which increased the proportion of its bonds with the compost organic compounds with the passage of time.

4. Irrespective of the duration of composting, nickel and lead were found to be associated most strongly with silicate minerals representing, in the discussed experimental conditions, the non-mobile fraction of heavy metals.

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ZMIANY CHEMICZNYCH POŁĄCZEŃ KADMU, NIKLU I OŁOWIU W KOMPOŚCIE WYTWORZONYM NA BAZIE OSADU ŚCIEKOWEGO

Katedra Gleboznawstwa i Ochrony Gruntów
Uniwersytet Przyrodniczy w Poznaniu

Abstrakt: Celem pracy było określenie zmian, jakie zachodzą w połączeniach chemicznych frakcji kadmu, niklu i ołowiu podczas kompostowania osadów z dodatkiem trocin i słomy w warunkach kompostowni otwartej. Do tego celu wykorzystano aerator ciągnikowy, który mieszał, rozdrabniał i napowietrzał kompost. Kompostowanie pryzmowe trwało 110 dni, a następnie komposty poddano dojrzewaniu (250 dni). Próbki do badań pobrano w 1, 54, 110 i 360 dniu doświadczenia, wykorzystując do analizy sekwencyjnej metali metodą BCR (Bureau Community of Reference).

Stwierdzono, że zmiany ilościowe i udziału poszczególnych frakcji metali dotyczyły głównie połączeń chemicznych frakcji rozpuszczalnych, a w niewielkim stopniu połączeń metali z minerałami krzemianowymi (frakcja rezydualna). W wyniku kompostowania w największym stopniu wzrastał udział połączeń kadmu we frakcjach wymiennej i łatwo rozpuszczalnej w kompoście dojrzałym, co należy uznać za proces niekorzystny. Z kolei następował spadek udziału połączeń chemicznych kadmu i ołowiu z substancją organiczną, a wzrost udziału takich połączeń w przypadku niklu.

Frakcja rezydualna w kompoście dojrzałym stanowiła w 38,2 % ogólnej zawartości kadmu, 63,1 % niklu i 84,9 % ołowiu.

Słowa kluczowe: kompost, połączenia chemiczne, kadm, nikiel, ołów

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Michał GĄSIOREK[1]

HEAVY METALS IN SOILS FROM DISTRICT PLAYGROUNDS IN THE NORTHERN PART OF KRAKOW

METALE CIĘŻKIE W GLEBACH OSIEDLOWYCH PLACÓW ZABAW PÓŁNOCNEJ CZĘŚCI KRAKOWA

Abstract: The research was conducted to assess the degree of pollution with Cd, Pb, Zn, Cu, Cr and Ni in the top layer of soils from district playgrounds in the northern part of Krakow. The analyses were conducted on soil material collected from 12 objects.

Determined values of chromium and nickel were similar to the values noted in soils unpolluted with these elements. The most of analyzed soils were classified to the soil with the natural contents of cadmium, lead and copper, although in some of them elevated contents of Cd, Pb or Cu were assessed and a slight pollution with Pb or Cu. A majority of the studied soils revealed elevated contents or a slight pollution with zinc. Dependence between Ni content and the amount of $\varnothing < 0.002$ mm fraction was highly significant. Slight relationship between Cd and Cu content and organic carbon content was also registered in the analyzed soils.

Keywords: playgrounds, urban soils, heavy metals, Krakow

In the urbanized areas soil plays a different role than in the natural environment. Among others it forms a substratum of recreational areas. District playgrounds provide opportunities for active spending of pass time. They differ with their sizes or the number and state of playground equipment anyway, all should be places of safe and healthy rest, which ought to be ensured by unpolluted soil. Therefore, the playground soil environmental monitoring is necessary and should involve also determining heavy metal content. Urban soil pollution with heavy metals was a subject of numerous investigations, however a definitely lesser number of those focused on playgrounds [1–3]. Soil affects human health directly or indirectly. The direct influence involves ingestion of soil, inhaling of soil dust and contact through the skin [4]. Especially young children, curious about the surrounding world and exploring the environment are exposed to the contact with contaminated soil. The examples are provided for

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[1] Department of Soil Science and Soil Protection, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone +48 12 662 4370, email: rrgasior@cyf-kr.edu.pl

lead polluted soils, where this element accumulation was observed in children's organisms [5].

The research was undertaken to assess the degree of pollution with heavy metals: Cd, Pb, Zn, Cu, Cr and Ni in the top layer of district playground soils located in the northern, left-bank side of Krakow.

Material and methods

Twelve playgrounds located in the northern part of Krakow: in Bronowice, Krowodrza, Srodmiescie and Nowa Huta districts were considered in the investigations (Fig. 1). They differed with their sizes, state in which playground equipment was maintained and turfing. Among the analyzed objects were small ones (eg the playground at Zwirki i Wigury Street) and very big ones (at Lotnicza Street). Depending on the size and spatial differentiation of the playgrounds, between 1 and 3 representative collective samples were taken from individual objects. A single collective sample consisted of 5 primary samples collected from the 0–20 cm soil layer using soil stick. In the laboratory the soil material was dried at room temperature and sifted through a plastic sieve with 2 mm mesh. Subsequently, soil texture [6], pH in 1 mol $\cdot$ dm^{-3} KCl solution, hydrolytic acidity [7] and the sum of exchangeable bases [8] was determined, organic carbon content was assessed with Tiurin method and total heavy metal contents using atomic absorption spectrometry after mineralization in concentrated nitric(V) and chloric(VII) acids [9].

The results were verified statistically. The interdependence between the contents of the analyzed heavy metal form and selected soil properties was determined by computing Spearman's rank correlation coefficient.

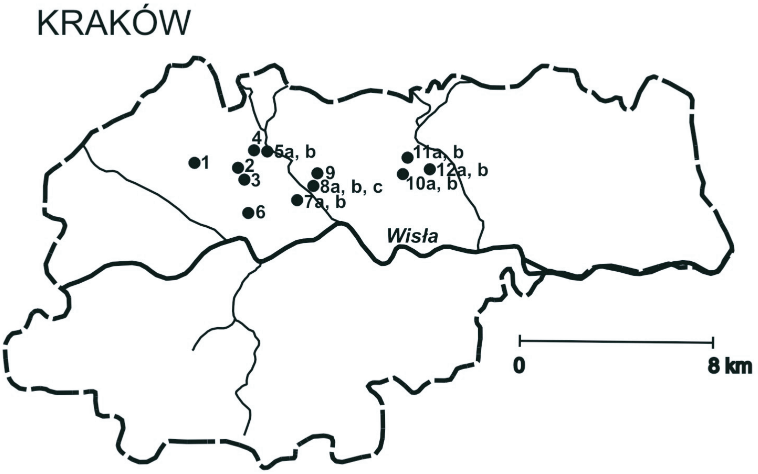

Fig. 1. Localisation of investigated playgrounds in the northern part of Krakow: 1 – Bronowicka St., 2 – Mazowiecka St., 3 – Grottgera Av., 4 – Fieldorfa-Nila St., 5a, 5b – Zdrowa St., 6 – Sikorskiego Sq., 7a, 7b – Kielecka St., 8a, 8b, 8c – Lotnicza St., 9 – Zwirki i Wigury St., 10a, 10b – Niepodleglosci housing estate, 11a, 11b – Kazimierzowskie housing estate, 12a, 12b – Gorali housing estate

Results and discussion

Results of basic soil properties assessments which affect heavy metal mobility and the contents of Cd, Pb, Zn, Cu, Cr and Ni were presented in Table 1.

Table 1

Basic properties and heavy metal contents in soils of the analyzed playgrounds

Point No.	pH_{KCl}	BS [%]	org. C [$g \cdot kg^{-1}$]	Fraction ∅ < 0.002 mm [%]	Cd	Pb	Zn	Cu	Cr	Ni
					[$mg \cdot kg^{-1}$]					
1	6.5	83.0	16.6	1	1.14	50.5	126.1	18.4	11.9	5.2
2	6.2	97.3	13.7	2	0.46	50.6	136.5	40.6	14.7	6.7
3	7.2	87.7	21.8	2	0.94	73.9	203.4	37.1	20.0	7.6
4	7.4	95.8	10.8	5	0.22	12.8	61.7	9.1	13.0	6.4
5a	7.2	94.8	14.5	3	0.47	46.0	144.5	25.9	10.7	6.7
b	7.2	95.8	11.1	5	0.47	31.6	185.6	13.9	11.4	6.5
6	6.8	90.5	12.8	6	0.55	106.0	214.1	20.8	12.7	8.1
7a	7.5	97.0	11.6	3	0.56	53.1	252.5	14.2	13.2	8.4
b	6.9	96.7	15.0	7	0.54	23.4	201.7	12.9	15.6	12.4
8a	7.1	96.7	12.3	10	0.30	3.0	68.2	9.1	10.6	10.7
b	7.3	98.1	13.4	9	0.25	8.9	104.1	10.8	12.9	10.7
c	7.2	97.8	11.9	13	0.09	9.1	69.0	10.0	17.2	11.9
9	7.1	97.2	25.1	6	0.29	13.7	131.6	13.6	17.2	9.1
10a	7.5	96.2	13.4	10	0.34	15.1	135.3	9.4	18.2	10.2
b	7.1	98.7	8.0	9	0.21	19.1	105.1	9.6	16.5	8.7
11a	6.2	87.6	13.8	13	0.35	15.6	104.2	10.0	19.3	11.9
b	7.1	92.7	15.9	10	0.46	24.5	119.6	10.5	17.8	11.0
12a	7.4	97.0	14.9	8	0.88	30.1	266.3	12.8	21.2	10.5
b	5.9	97.7	7.2	11	0.35	17.7	108.0	8.9	13.9	8.2

Texture of the analyzed playground soils depended on the parent rock, but was also the result of anthropogenic effect. The area of Krakow situated north of the Vistula River is composed of loesses and non-loess deposits [10]. The influence of natural factors on the soil texture is most clearly visible on the playgrounds in Nowa Huta (objects 10–12) where soils, similarly as loess, used to be silts. However, in the past these playgrounds used to be construction sites or were located in their vicinity, which resulted in introducing gravel, sand or more finely granulated fraction into the soils. It is evidenced by diversified texture on the playgrounds from which more than one soil sample was taken (eg objects 5 and 8). Beside silts or loamy silts the investigated soils revealed the texture of strong loamy silty sands, strong loamy sands, light loamy sands and light silty loams. They also considerably differed with the content of ∅ < 0.002 mm fraction; the soils located in the western part of the studied area contained apparently smaller quantities of clay than the ones in the eastern part (Fig. 1). The investigated soils were characterized by pH between 5.9 and 7.5 but generally higher than 7.0. It allowed to classify a majority of them to alkaline or neutral soils, and only four were counted among slightly acid soils. A substantial share of alkaline or neutral soils in cities, particularly in Krakow, was also reported by Pasieczna [11]. A considerable diversification in pH was observed among the soil samples collected from the playgrounds at Kazimierzowskie and particularly at Gorali housing estates (objects 11 and 12), which evidences a point introduction of materials containing alkaline components. The obtained values of base saturation [BS] also assume very high values, approximate to or exceeding 90 %. Organic carbon contents in the analyzed soils was diversified and fluctuated from 7.2 to 25.1 $g \cdot kg^{-1}$ (on average 13.9 $g \cdot kg^{-1}$).

Anthropogenic effect either had no effect or only to a slight degree influenced the contents of chromium and nickel in the top soil layer of playgrounds located in the northern part of Krakow. These elements content oscillated within a relatively narrow range, ie from 10.6 and 21.2 mg Cr $\cdot kg^{-1}$ (on average 15.1 $mg \cdot kg^{-1}$) and 5.2–12.4 $mg \cdot kg^{-1}$ Ni (on average 9.0 $mg \cdot kg^{-1}$). These amounts are similar to registered in soil unpolluted with these elements [12]. Also soil contents of cadmium, lead and copper, assessed according to heavy metal soil pollution classification suggested by ISSPC (IUNG) [13], allow to count most of the analyzed soils to the class with natural contents (0^o of pollution) of these elements. However, soils from the playgrounds at Bronowicka and Mazowiecka Streets, Grottgera Avenue, Sikorskiego Square or Kielecka Street revealed elevated content of cadmium (I^o of pollution). Elevated lead contents (I^o of pollution) occurred in the soils of the playgrounds at Mazowiecka and Kielecka Streets (point 7a), whereas slight Pb pollution (II^o of pollution) was detected in soil of the playground at Sikorskiego Square. Copper contents were elevated (I^o of pollution) only in soils of the playgrounds situated at Grottgera Avenue and Zdrowa Street on the point 5a, whereas the playground soil at Mazowiecka Street was slightly polluted. Zinc was the only metal whose content (except for soil from points 4, 8a and 8c) was higher than considered normal [13] and reached 266.3 $mg \cdot kg^{-1}$. In most of the analyzed soils elevated zinc content was noted or a slight pollution was observed in the soils from playgrounds located at Mazowiecka Street, Grottgera Avenue, Sikorskiego Square and Kielecka Street. According to the Regulation of Minister of the Environment on the soil quality standards and earth quality standards [14] the admissible contents of Cd, Pb, Zn, Cu, Cr or Ni were not exceeded in any of the investigated playground soils.

Conducted statistical analysis revealed weak relationships between organic carbon content and the quantity of cadmium and copper (Table 2). The dependence between the content of $\varnothing < 0.002$ mm fraction and nickel content was highly significant. Also significant dependencies occurred between this fraction content and contents of the other heavy metals (except chromium), however, due to a negative value of correlation coefficient these should be considered accidental. It evidences human impact on the texture of the analyzed soils and is contrary to fixed opinions on the relationship between clay fraction content and amount of heavy metals [12]. The other relationships were statistically insignificant (Table 2).

Table 2

Spearman's rank correlation coefficients (r) between heavy metal contents and selected properties of the analyzed soils (n = 19)

Property	Cd	Pb	Zn	Cu	Cr	Ni
pH KCl	–0.068	–0.117	0.152	–0.061	0.078	–0.065
Org. C	0.479*	0.239	0.326	0.526*	0.358	0.153
∅ < 0.002	–0.582**	–0.679**	–0.508*	–0.790***	0.313	0.764***

* $p \le 0.05$, ** $p \le 0.01$, *** $p \le 0.001$.

The content of the analyzed heavy metals in playground soils located in the northern part of Krakow usually remains on an approximate or even lower level than in the variously used soils of Krakow [11, 15, 16]. Higher contents of particularly zinc and lead occurred in the areas earlier and more intensively urbanized, as eg Sikorskiego Square, which corroborates the research of Ljung et al [1]. Generally, the determined heavy metal contents are not alarming. Slight pollution of the soils with zinc and lead may seem disturbing. It was registered on the playgrounds poorly turfed or practically devoid of vegetation, such as the ones at Grottgera Avenue or Kielecka Street. Children while playing there may carry soil particles to alimentary tract because of dirty hands [2, 4]. They may be also more exposed to inhaling soil dust due to their low height. Therefore it is so important to maintain greenery, particularly lawns on playgrounds, in good condition because of their isolating function. It also affects humus content in soil, the soil structure and therefore the air-water relationships.

Conclusions

1. Soils of district playgrounds in the northern part of Krakow were not polluted with chromium or nickel.
2. Most of the analyzed soils revealed natural (0^o of pollution) contents of cadmium, lead and copper acc. to ISSPC criteria, but soils with elevated (I^o of pollution) contents of Cd, Pb and Cu were also registered, as well as single soils slightly polluted (II^o of pollution) with Pb or Cu each.
3. Elevated contents of zinc were found in most soils, whereas in several also slight pollution with this element was observed.
4. Highly significant relationship was noted between the nickel content and share of ∅ < 0.002 mm fraction and weak relationship between cadmium and copper contents and organic carbon content.
5. Greenery on playgrounds, especially lawns should be maintained in good condition, since in the event of elevated heavy metal contents they will limit the direct contact between soil and child's organism.

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METALE CIĘŻKIE W GLEBACH OSIEDLOWYCH PLACÓW ZABAW PÓŁNOCNEJ CZĘŚCI KRAKOWA

Katedra Gleboznawstwa i Ochrony Gleb
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Przeprowadzone badania miały na celu ocenę stopnia zanieczyszczenia Cd, Pb, Zn, Cu, Cr i Ni wierzchniej warstwy gleb osiedlowych placów zabaw północnej części Krakowa. Badania przeprowadzono na materiale glebowym pobranym z 12 obiektów.

Oznaczone zawartości chromu i niklu były podobne do występujących w glebach niezanieczyszczonych tymi pierwiastkami. W przypadku kadmu, ołowiu i miedzi większość badanych gleb zaliczono wg kryteriów IUNG do gleb o naturalnej ich zawartości (0^o zanieczyszczenia), chociaż w kilku z nich wystąpiła podwyższona zawartości Cd, Pb lub Cu (I^o zanieczyszczenia) oraz słabe zanieczyszczenie Pb lub Cu (II^o zanieczyszczenia). Większość badanych gleb charakteryzowała się zwiększoną zawartością lub słabym zanieczyszczeniem cynkiem. Stwierdzono statystycznie istotną zależność między zawartością Ni a ilością frakcji $\varnothing < 0.002$ mm. Wystąpiła również słaba zależność między zawartością Cd i Cu a zawartością węgla organicznego w analizowanych glebach.

Słowa kluczowe: place zabaw, gleby miejskie, metale ciężkie, Kraków

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Małgorzata HAWROT-PAW[1] and Magdalena CZAPLA

CELLULOLYTIC ACTIVITY OF MICROFLORA IN SOIL CONTAMINATED WITH AROMATIC HYDROCARBONS

CELULOLITYCZNA AKTYWNOŚĆ GLEBY ZANIECZYSZCZONEJ WĘGLOWODORAMI AROMATYCZNYMI

Abstract: This study evaluated the influence of contamination with aromatic hydrocarbons on the efficacy of cellulose decomposition with the use of soil cellulolytic microorganisms. In the experiments we used the monoaromatic hydrocarbons from BTEX group (benzene, toluene, ethylobenzene and xylene – a mixture) and polycyclic compounds (naphthalene and anthracene) used in the following concentrations: 100, 1.000 and 10.000 mg · kg^{-1} d.m. of soil.

We found out that usually the presence of aromatic hydrocarbons stimulated the cellulolytic activity of soil microflora – the higher activity was noted in the soil contaminated with PAH (anthracene). The percentage of cellulose decomposition was increased along with the increase of monoaromatic hydrocarbon dosage (except toluene); a similar dependence was not noted for polycyclic aromatic hydrocarbons (PAH).

Keywords: cellulolytic activity, microorganisms, aromatic hydrocarbons

The living organisms are poisoned with substances of different origin. Aromatic hydrocarbons are a very harmful group of compounds, as they have a carcinogenic effect. The disturbance of balance between creation and decomposition of polycyclic aromatic hydrocarbons in the natural environments, including soil, causes the increase of concentration of xenobiotics in ecosystems, and as a result of that, disturbance of biologic balance [1].

The soil microorganisms, thanks to their numerous biologic properties and biochemical abilities, are a necessary factor for metabolism. Participating in different biochemical processes they play an important role in functioning of all of the land ecosystems. The result of their activity is not only mineralization and humification of different organic compounds (including synthesis of humus – the largest bioenergetic potential of soils), but also activation of many mineral compounds, having basic meaning for the life of plants and soil animals [2, 3]. The petroleum hydrocarbons

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[1] Department of Microbiology and Environmental Biotechnology, West Pomeranian University of Technology, ul. Słowackiego 17, 71–434 Szczecin, Poland, phone +48 91 44 96 423, email: Malgorzata.Hawrot-Paw@zut.edu.pl

introduced to the soil exert an influence on soil respiration, microbial biomass carbon or enzyme activities [4–6].

In the accessible literature there is not too much data concerning the influence of aromatic hydrocarbons on the activity of particular groups of soil microorganisms, which are responsible for stabilization – homeostasis of ecosystem, through composition and decomposition of organic compounds in soil, and also through release and storage of foods [7], while enzymatic reactions are a base of soil metabolism, they decide about the rate and direction of metabolic changes, that take place in the soil [8], have been used to estimate ecosystem functioning and soil fertility [9]. Microbial cellulolytic activities in soil are important indicators of soil health and quality [10, 11].

The aim of this study, considering a very important role of microflora in a proper functioning of soil environment, was evaluation of the influence of chosen monoaromatic hydrocarbons and polycyclic hydrocarbons on the cellulolytic activity of soil microorganisms.

Materials and methods

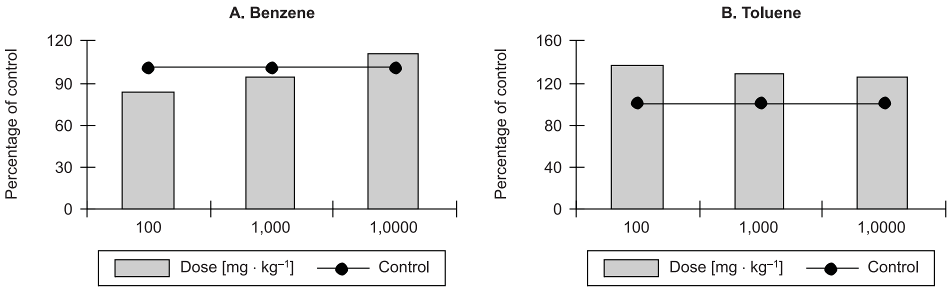
For our studies we collected some soil samples from Ostoja situated near by Szczecin. It was a clay soil, black ground type. The material was collected from the depth of 0–15 cm of the humus level. After transportation to the laboratory, we dried and ground the soil using the riddle with 2 mm orifices. The material was brought to 60 % MPW. This humidity was constant for the entire time of experiment, in case it was necessary the losses were replenished with distilled water.

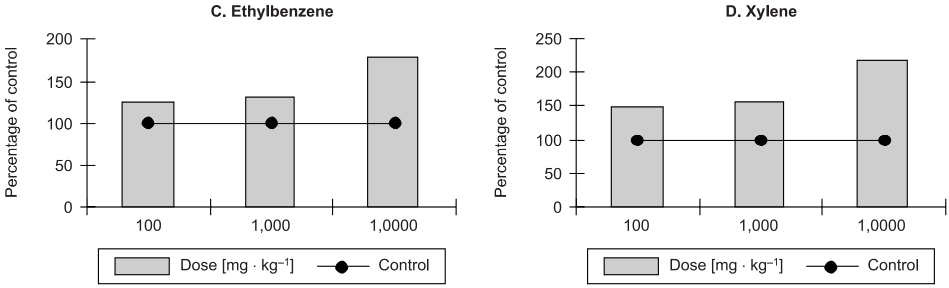
The material was divided into small samples, each one of 300 g, and placed in polyethylene containers. Later on, the samples were contaminated with the following doses of hydrocarbons: 100, 1,000 and 10,000 mg $\cdot$ kg^{-1} d.m. of soil. In the experiments we used the monoaromatic hydrocarbons from BTEX group (benzene, toluene, ethylobenzene and xylene – a mixture) and polycyclic aromatic compounds (naphthalene and anthracene). One of the samples, not contaminated with the hydrocarbons was left as a control sample. In order to assess the cellulolytic activity we inserted the cellulose samples into the bags with soil. Each bag had 6 cardboards of the 2 × 2 cm dimensions and the average weight of 350 mg. The soil samples were incubated at room temperature (± 20 ^{o}C).

The level of cellulose decomposition was evaluated based on the differences of weight between the cardboard inserted into the contaminated soil and after finishing of the experiment – a modified method according to Kuzniar [12]. After its taking out, the cellulose cardboard was dried at a temperature of 105 ^{o}C, until receiving of a constant weight. The analysis was carried out on the day of contamination of the soil with hydrocarbons and later after 7, 14, 28, 56 and 112 days of incubation. The study results were analysed statistically using two-way analysis of variance.

Results

Along with the increase of benzene dosage in the studied objects we could observe the increase of activity of cellulolytic microorganisms, but for the dose of 100 and 1,000 mg · kg^{-1} d.m. of soil the value was lower compared with the control object, and it was 16 and 7 %. After use of the highest dose (10,000 mg · kg^{-1} d.m. of soil) we noted the increase of activity of 10 % compared with the control (Fig. 1A).





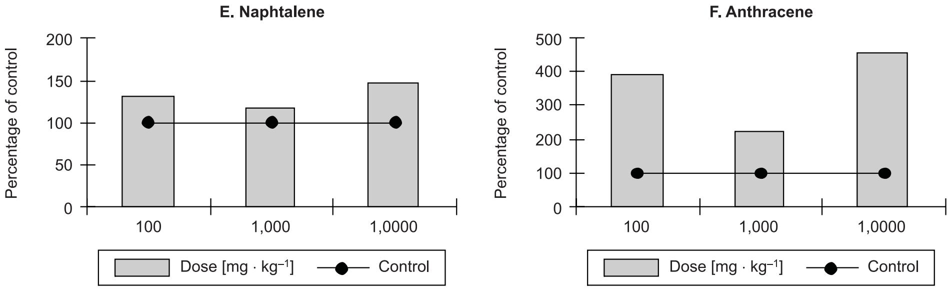


Fig. 1. The influence of hydrocarbons on the cellulolytic activity of soil microorganisms expressed as a control percentage

Toluene implemented to the soil caused increase of activity of cellulose decomposing microorganisms compared with the control, however the activity decreased along with the increase of hydrocarbon concentration (Fig. 1B). Under the dosage of 100 mg · kg^{-1} d.m. of soil the weight loss was 90 mg, while the dose of 10,000 mg · kg^{-1} d.m. of soil caused a loss which was 20 mg lower.

The addition of ethylbenzene caused increase of cellulolytic activity compared with the control, and the higher the dose was the higher the increase was. For the concentration of 10,000 mg · kg^{-1} d.m. of soil the activity was 80 % higher compared to the control, and for the dose of 100 mg · kg^{-1} d.m. of soil – 25 % (Fig. 1C).

After implementation of xylene into the soil we observed a similar reaction. Along with the increase of hydrocarbon's dosage we observed an increasing loss of weight of the cellulose cardboard. In case of xylene we could also observe the increase of cellulolytic activity. For the highest concentration the increase of cellulose decomposing microorganisms was over 100 % compared with the control object (Fig. 1D).

In all of the experiments with naphthalene, just like in case of hydrocarbons from BTEX group, we observed the stimulation of activity of cellulolytic microorganisms, however in this case we did not reveal any dependence between the enzymatic activity and increasing concentration of hydrocarbons – the lowest activity was noted in the object with the dose of 1,000 mg · kg^{-1} d.m. of soil (Fig. 1E). The weight depletion for this dose was 65 mg – which is 15 mg less than in case of the highest dose (the increase of activity for this object was 45 % above the control sample).

Anthracene implemented to the soil also stimulated the cellulolytic activity of microorganisms. For the dose of 10,000 mg · kg^{-1} d.m. of soil the activity increased over 350 % compared with the control (Fig. 1F). The weight depletion for this object was almost 200 mg. The lowest activity of microorganisms decomposing cellulose was assessed for the concentration of 1,000 mg · kg^{-1} d.m. of soil – the loss of weight for this dose was 100 mg (the increase of activity was 120 % compared with the control object).

The carried out statistical analysis showed a significant effect of the hydrocarbons dose and incubation days on the cellulolytic activity, but no significant effect of the interaction of both examined factors (Table 1).

Table 1

Results of statistical analysis for the cellulolytic activity of soil microorganisms

Factor	Number of independent variables	Mean square sum.	Number of independent variables for error	Mean square sum for error	F value	P value
1	5	0.092522	306	0.001524	60.69422	0.00*
2	2	0.019119	306	0.001524	12.54230	0.00*
1 · 2	10	0.001201	306	0.001524	0.78787	0.64

Factors: 1 – measurement period, 2 – dose of hydrocarbons
* – a significant effect of a factor ($p < 0.05$).

Discussion and conclusions

The results of this study illustrate a significant influence of the aromatic hydrocarbons used in the experiments on the activity of the soil microorganisms. Also Zablocka-Godlewska and Buczkowska-Wesolowska [13] assessed that the hydrocarbons implemented to the natural environment like soil, can have a very variable influence on the biologic balance as well as on the quantity and quality changes of microorganisms.

It is assessed that usually the presence of aromatic hydrocarbons in soil stimulated the cellulolytic activity of microorganisms. A similar situation after implementation of the diesel fuel, which is a mixture of hydrocarbons, was observed by Daca et al [14] – the percentage of decomposed cellulose in soil was increased of 40 % compared with the control. Higher decomposition rates of organic matter in the fuel polluted soil than in the uncontaminated was also reported by Griffiths et al [15]. Cellulose is decomposed by aerobic bacteria, anaerobic bacteria, thermo- and mesophylic bacteria, different kinds of fungi, actinomycetales and protozoans, and for most of those organisms cellulose is one of the possible sources of carbon and energy [8]. Therefore such reaction could have been the result of activation of soil microflora influenced by the additional source of carbon.

For benzene, ethylbenzene and xylene the activity increased along with the increase of hydrocarbon concentration. Activities of many soils enzymes are often correlated with organic C content [16, 17], but we did not note any significant dependence after the use of polycyclic aromatic hydrocarbons – the lowest activity to decompose the cellulose was observed for the dose of 1,000 mg $\cdot$ kg^{-1} d.m. of soil. No significant relationship between the concentration of hydrocarbons and cellulose decomposition was observed by Mendelssohn and Slocum [18]. Despite of the dosage of hydrocarbon, in the objects contaminated with naphthalene as well as with anthracene, the cellulose decomposition was more effective than in control sample. Few studies suggest that decomposition should increase with petroleum hydrocarbon addition [16, 19], but other available results of investigation concerning of cellulose decomposition are not synonymous. In the studies of Maliszewska-Kordybach et al [20] the decrease of enzymatic activity due to PAH was observed on the level of 10 mg $\cdot$ kg^{-1} d.m. of soil. Inhibition of cellulolytic activity was observed also by other authors. Małachowska-Jutsz et al [21] found out that the activity of cellulase remained constant for the entire period of experiment and it was about 95–97.5 % of the control sample. The authors found that the activity did not depend of the kind and dosage of xenobiotic. Similar results had also reported Surygala [22] and Przystas et al [8].

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CELULOLITYCZNA AKTYWNOŚĆ GLEBY ZANIECZYSZCZONEJ WĘGLOWODORAMI AROMATYCZNYMI

Katedra Mikrobiologii i Biotechnologii Środowiska
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

Abstrakt: W pracy określano wpływ zanieczyszczenia węglowodorami aromatycznymi na efektywność rozkładu błonnika przy udziale celulolitycznych mikroorganizmów glebowych. W doświadczeniach wykorzystano węglowodory monoaromatyczne z grupy BTEX (benzen, toluen, etylobenzen i ksylen – mieszanina) oraz wielopierścieniowe (naftalen i antracen), które stosowano w stężeniach 0, 100, 1000 i 10 000 g · kg^{-1} s.m. gleby.

Stwierdzono, że na ogół obecność węglowodorów aromatycznych stymulowała celulolityczną aktywność mikroflory glebowej – większą aktywność odnotowano w glebie zanieczyszczonej naftalenem i antracenem. Procent rozkładu błonnika zwiększał się wraz ze wzrostem dawki węglowodorów monoaromatycznych (z wyjątkiem toluenu); podobnej zależności nie odnotowano dla węglowodorów wielopierścieniowych.

Słowa kluczowe: aktywność celulolityczna, mikroorganizmy, węglowodory aromatyczne

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Stanisław KALEMBASA[1] and Agnieszka GODLEWSKA[1]

INFLUENCE OF SEWAGE SLUDGE AND LIMING ON COPPER, ZINC AND IRON CONTENTS IN ITALIAN RYEGRASS (*Lolium multiflorum* Lam.)

ODDZIAŁYWANIE OSADÓW ŚCIEKOWYCH I WAPNOWANIA NA ZAWARTOŚĆ MIEDZI, CYNKU I ŻELAZA W ŻYCICY WIELOKWIATOWEJ (*Lolium multiflorum* Lam.)

Abstract: The paper presents results from a study dealing with the evaluation of sewage sludge application on light and medium soils as well as liming on Cu, Zn, and Fe content in Italian ryegrass.

Metals contents found in sludge allowed for their agricultural application. Experimental factors had significant influence on copper, zinc, and iron contents at plants. Fertilization using sewage sludge considerably affected the content of Cu, Zn, and Fe in Italian ryegrass. Copper and iron levels in plants grown on light soil increased significantly. Liming differentiated Cu and Fe contents not explicitly, but it considerably decreased Fe content in studied grass species.

Keywords: sewage sludge, copper, iron, zinc, liming, *Lolium multiflorum* Lam.

Waste organic materials such as sewage sludge, have been recently more commonly applied for agricultural purposes. That way of their utilization is consistent with EU policy that accepts their return to the environment. Sewage sludge one may consider as organic fertilizer with high content of organic matter and nutrients [1–3] such as nitrogen or phosphorus for plants [4, 5]. However, natural utilization of these materials meets many obstacles, eg chemical contamination due to excess of heavy metals and toxic organic substances [6, 7]. These contaminants may cause changes in soil fertility, decrease plant yielding, and affect their quality [8]. Therefore, the knowledge of the chemical composition of sewage sludge and its appropriate application is the basis for its utilization [9].

The aim of the present study was to evaluate copper, zinc, and iron contents in sewage sludge as well as the influence of sludge application and liming on these metals contents in Italian ryegrass.

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[1] Department of Soil Science and Plant Nutrition, University of Podlasie, ul. B. Prusa 14, 08–110 Siedlce, Poland, phone +48 25 643 1287 (88), email: kalembas@ap.siedlce.pl, godlewskaa1@o2.pl

Material and methods

A two-year pot experiment was set in a greenhouse in completely randomized pattern. It consisted of the following factors:

I. soil type (heavy loamy sand, silty sandy loam),
II. liming (without or with according to hydrolytic acidity $H_h = 1$),
III. fertilization (manure and sewage sludge from two purification plants).

Sewage sludge applied in the experiment originated from industrial and municipal sewage purification plant in Siedlce (it was subjected to methane fermentation and partially dehydrated in a press at the end of the processing), as well as from a purification plant of Poultry Works "Drosed" in Siedlce. Fertilization using sewage sludge at the amount of 15 % of fresh matter in relation to the soil quantity was applied only once. The action of both sludge types was compared with the farmyard manure applied at the same rates and dates as sewage sludge.

Annual ryegrass (*Lolium multiflorum* Lam.) was used as the test plant, which was subjected to three cuts during the vegetation season. The harvested biomass was dried, ground and ashed. Total Cu, Zn and Fe contents were determined by means of the ICP-EAS technique in extracts after ash dissolution. Plant material was combusted in a muffle furnace at 450 ^{o}C with gradually increased temperature. Next, mineralized samples were dissolved in HCl solution (1:1 with water) and evaporated till dryness. Such prepared sample solutions were transferred to measure flasks with 10 % HCl through hard filter paper. Total amounts of Cu, Zn, and Fe in sewage sludge were also determined by means of ICP-EAS after dry digestion.

Results were statistically processed by applying the analysis of variance and using F-Fisher-Snedecor's test with a help of F.R. Anal var. 4.1 software (acc. to Franciszek Rudnicki), while values of $LSD_{0.05}$ were calculated according to Tukey's test.

Results and discussion

The contents of Cu, Zn, and Fe in sewage sludge applied in the experiment are presented in Table 1.

Table 1

Basic properties of sewage sludge and farmyard manure

Organic materials	pH_{H_2O}	Organic carbon [$g \cdot kg^{-1}$ d.m.]	Cu	Zn	Fe
			[$mg \cdot kg^{-1}$ d.m.]		
Sewage sludge form Siedlce	6.7	371	30.0	318	3 272
Sewage sludge from "Drosed"	7.2	520	54.6	214	15 967
Farmyard manure	6.9	473	15.6	187	1 952

Contents of Cu and Zn were at similar levels in both tested materials; however, iron content in sludge from "Drosed" was five times higher as compared with that from purification plant in Siedlce, which was associated with the application of $FeSO_4$ as flocculent during sewage purification process. However, total contents of studied metals in the sludge did not exceed the thresholds norms for their agricultural application [9].

Copper content of Italian ryegrass (Table 2) varied in the range from 4.07 mg · kg^{-1} d.m. in the plants of 3rd cut from control object in the second experimental year to 22.2 mg · kg^{-1} d.m. in the biomass harvested in the 1st cut in the first year of experiment from the object fertilizer manure.

Table 2

Content of Cu [mg · kg^{-1} d.m.] in *Lolium multiflorum* Lam. in the 1st and 2nd year of study

Liming	Kind of soil											
	Heavy loamy sand						Silty sandy loam					
	Cuts	Fertilization				Mean	Cuts	Fertilization				Mean
		A*	B	C	D			A	B	C	D	
The 1st year of experiment												
0	I	9.78	13.74	15.41	20.51	14.86	I	9.31	13.33	12.99	16.19	12.96
	II	9.50	13.00	12.46	13.00	11.99	II	9.89	13.25	9.65	16.00	12.20
	III	9.94	10.89	14.32	17.80	13.24	III	9.55	13.2	7.70	16.34	11.70
	Mean	9.74	12.54	14.06	17.10	13.35	Mean	9.58	13.26	10.11	16.18	12.29
Ca	I	12.47	22.21	13.98	15.03	15.92	I	11.05	18.76	14.07	18.11	15.50
	II	10.42	18.16	14.81	17.22	15.15	II	8.47	15.55	11.90	14.10	12.51
	III	8.68	16.28	10.88	19.00	13.71	III	9.73	12.73	12.32	13.04	11.96
	Mean	10.52	18.88	13.22	17.08	14.93	Mean	9.75	15.68	12.76	15.08	13.32
Mean		10.13	15.71	13.64	17.09	14.14	Mean	9.67	14.47	11.44	15.63	12.81
The 2nd year of experiment												
0	I	9.90	12.58	8.40	10.09	10.24	I	8.06	14.76	8.61	12.54	10.99
	II	5.00	11.80	9.16	9.55	8.88	II	6.47	11.6	11.09	10.14	9.83
	III	4.07	11.44	10.18	7.11	8.20	III	4.77	8.50	10.25	8.54	8.02
	Mean	6.32	11.94	9.25	8.92	9.11	Mean	6.43	11.62	9.98	10.41	9.61
Ca	I	11.91	11.32	8.15	13.51	11.22	I	12.51	7.44	8.93	10.44	9.83
	II	10.00	12.95	7.68	7.00	9.41	II	4.91	7.66	10.84	8.82	8.06
	III	10.68	8.04	8.29	8.49	8.88	III	6.22	7.29	9.04	8.17	7.68
	Mean	10.86	10.77	8.04	9.67	9.84	Mean	7.88	7.46	9.60	9.14	8.52
Mean		8.59	11.36	8.65	9.30	9.48	Mean	7.16	9.54	9.79	9.78	9.07

*A – control, B – farmyard manure, C – sludge from Siedlce, D – sludge from Drosed.

		1st year	
LSD$_{0.05}$	I cut	II cut	III cut
for fertilization	0.879	0.943	1.051
for soil	0.467	0.501	0.559
for liming	0.467	0.501	ns
for fertilization x soil	ns	1.333	1.486
for fertilization x liming	1.243	1.333	1.486
for liming x soil	0.661	0.709	ns
		2nd year	
for fertilization	0.870	0.711	0.714
for soil	ns	ns	0.380
for liming	ns	ns	ns
for fertilization x soil	ns	1.006	1.010
for fertilization x liming	1.231	1.006	1.010
for liming x soil	0.654	0.535	0.537

Explanation for Tables 2 to 4: ns – non significant

In both years of experiments, the studied factors had significantly influenced copper content of tested plants. Organic fertilization, sludge and farmyard manure, considerably increased the level of tested element in ryegrass in the first and second years, which was consistent with results of other authors [10, 11]. Significantly higher copper content was also found in plants grown on light soil in the first year, while in the second year, the soil type had no significant impact on copper amounts in Italian ryegrass. Liming affected copper uptake by plants in not explicit way. Liming considerably increased its concentration in plants of the 1st and 2nd cuts of the first year. Thus, it can be supposed that the effect of liming has not been manifested yet in the first experimental year. In the second year, liming significantly decreased Cu content at the 2nd cut.

According to Kabata-Pendias and Pendias [12], zinc content in grasses ranges from 3.7 up to 292 mg · kg^{-1} d.m.. Results obtained in the current work also oscillated within wide range (Table 3), which is also confirmed by other author's research [13], as well as thanks to the statistical analysis, indicating significant influence of all studied factors on zinc concentration in Italian ryegrass. According to Kabata-Pendias and Pendias [12], the addition of municipal wastes causes the increase of mobile zinc forms content and their desorption decreases proportionally to the soil acidity increase, as confirmed by present study.

Fertilization using sludge from Siedlce significantly elevated Zn content in all grass cuts which can be attributed to the chemical composition of the sludge. Applying sludge from "Drosed" considerably increased zinc concentration only at 2nd cut grass in the second experimental year. The soil type differentiated Zn content in Italian ryegrass in not univocal manner. In the first year of experiment, significantly higher content of zinc was determined in the biomass of grass harvested in 1st cut cultivated on the medium soil that light once, but in the biomass of grass harvested as 2nd and 3rd cut from all object applied on light that medium soil. In the second year, significantly higher of zinc content was found only in 1st cut Italian ryegrass cultivated on the light soil. Liming caused univocal zinc content decrease at all cuts of the plants. Therefore, it can be supposed that soil acidity has a detrimental influence on its uptake by plants.

Factors studied in the experiment significantly differentiated iron content in plants (Table 4). The highest mean value of Fe (271.3 mg · kg^{-1} d.m.) was recorded in Italian ryegrass after application of sludge from "Drosed", which should be associated with high iron amounts in that organic material. Iron content in particular cuts, except from the 3rd cut in the second experimental year, was significantly higher, due to sewage sludge application, which proves a gradual mineralization of organic matter within the sludge. Considerably a higher level of the studied metal was found in plants grown on medium soil in the first year and 1st cut of the second experimental year. Liming significantly elevated iron concentration in grass, except from the last cut in the second year.

Fertilization using sewage sludge decidedly affected the increase of Cu, Zn, and Fe contents in Italian ryegrass. Also soil type exerted significant influence on these metals uptake by plants. Significantly high content of Cu and Fe obtained in plants harvested from objects with light than medium soil what could be explained by low ability of light soil to absorb these metals and therefore more of those metals were in soluble forms.

Table 3

Content of Zn [mg · kg^{-1} d.m.] in *Lolium multiflorum* Lam. in the 1st and 2nd year of study

Liming	Kind of soil											
	Heavy loamy sand						Silty sandy loam					
	Cuts	Fertilization				Mean	Cuts	Fertilization				Mean
		A*	B	C	D			A	B	C	D	
The 1st year of experiment												
0	I	56.9	82.2	172.3	88.6	100.0	I	52.4	123.4	155.5	98.7	107.5
	II	90.2	138	190.6	107.9	131.7	II	92.8	91.9	134.9	114.3	108.5
	III	89.1	67.4	220.0	98.9	118.9	III	38.4	103.7	157.2	103.3	100.7
	Mean	78.7	95.9	194.3	98.5	116.9	Mean	61.2	106.3	149.2	105.4	105.5
Ca	I	65.7	76.4	172.4	76.3	97.7	I	66.1	84.8	152.7	96.0	99.9
	II	104.6	120.7	183.1	107.5	129.0	II	96.5	101.3	130.3	100.2	107.1
	III	55.6	64.8	192.9	95.7	102.3	III	60.4	70.7	149.6	99.5	95.1
	Mean	75.3	87.3	182.8	93.2	109.7	Mean	74.3	85.6	144.2	98.6	100.7
Mean		77.0	91.6	188.6	95.9	113.3	Mean	67.8	96.0	146.7	102.0	103.1
The 2nd year of experiment												
0	I	147.8	128.2	226.1	142.3	161.1	I	128.3	135.1	294.8	128.2	171.6
	II	55.7	65.3	236.1	60.3	104.1	II	64.2	37.8	174.2	72.2	87.1
	III	28.3	50.9	161.1	80.1	80.1	III	42.3	59.2	142.1	48.7	73.1
	Mean	77.3	81.5	207.8	94.2	115.1	Mean	78.3	77.4	203.7	83.0	110.6
Ca	I	136.3	75.6	170.1	101.7	120.9	I	131.0	95.9	201.8	132.9	140.4
	II	47.1	52.6	134.4	43.6	69.4	II	56.0	31.7	195.1	62.2	86.3
	III	52.6	28.4	110.6	57.3	62.2	III	42.9	56.1	127.4	58.2	71.2
	Mean	78.7	52.2	138.4	67.5	84.2	Mean	76.6	61.2	174.8	84.4	99.3
Mean		78.0	66.9	173.1	80.9	99.7	Mean	77.5	69.3	189.3	83.7	105.0

*A – control, B – farmyard manure, C – sludge from Siedlce, D – sludge from Drosed.

1st year

LSD$_{0.05}$	I cut	II cut	III cut
for fertilization	6.237	5.769	9.556
for soil	3.317	3.068	5.081
for liming	3.317	ns	5.081
for fertilization x soil	8.821	8.159	13.515
for fertilization x liming	8.821	8.159	ns
for liming x soil	ns	ns	7.186

2nd year

for fertilization	6.653	7.667	7.277
for soil	3.537	ns	ns
for liming	3.537	4.077	3.869.
for fertilization x soil	9.408	10.843	10.291
for fertilization x liming	9.408	10.843	10.291
for liming x soil	5.003	5.766	5.472

Table 4

Content of Fe [mg · kg^{-1} d.m.] in *Loilium multiflorum* in the 1st and 2nd year of study

Liming	Kind of soil											
	Heavy loamy sand						Silty sandy loam					
	Cuts	Fertilization				Mean	Cuts	Fertilization				Mean
		A*	B	C	D			A	B	C	D	
The 1st year of experiment												
0	I	196.3	289.4	241.1	312.7	259.9	I	193.3	210.4	238.4	264.1	226.6
	II	230.8	211.6	206.1	315.9	241.1	II	182.3	242.7	195.0	250.9	217.7
	III	219.2	166.4	223.1	223.2	208.0	III	122.2	250.9	154.6	192.3	180.0
	Mean	215.4	222.5	223.4	283.9	236.3	Mean	165.9	234.7	196.0	235.8	208.1
Ca	I	211.5	364.8	238.7	309.0	281.0	I	231.9	310.2	329.8	265.6	284.4
	II	249.3	295.6	230.8	228.8	251.1	II	195.6	289.1	216.2	244.2	236.3
	III	193.3	232.0	183.4	273.2	220.5	III	142.8	169.7	220.0	273.6	201.5
	Mean	218.0	297.5	217.6	270.3	250.9	Mean	190.1	256.3	255.3	261.1	240.7
Mean		216.7	260.0	220.5	277.1	243.6	Mean	178.0	245.5	225.7	248.5	224.4
The 2nd year of experiment												
0	I	233.9	272.1	260.1	406.7	293.2	I	203.4	279.0	247.4	274.6	251.1
	II	216.9	250.0	245.6	224.8	234.3	II	209.3	151.9	247.8	286.4	223.9
	III	226.1	241.0	197.7	235.7	225.1	III	276.2	341.9	234.3	217.8	267.6
	Mean	225.6	254.4	234.5	289.1	250.9	Mean	229.6	257.6	243.2	259.6	247.5
Ca	I	295.5	280.0	295.8	318.2	297.4	I	281.1	259.9	280.3	325.3	286.7
	II	237.2	273.3	285.6	310.0	276.5	II	270.3	328.5	273.9	257.7	282.6
	III	272.0	169.5	289.2	202.3	233.3	III	207.1	188.9	191.1	292.1	219.8
	Mean	268.2	240.9	290.2	276.8	269.1	Mean	252.8	259.1	248.4	291.7	263.0
Mean		246.9	247.7	262.4	283.0	260.0	Mean	241.2	258.4	245.8	276.7	255.5

*A – control, B – farmyard manure, C – sludge from Siedlce, D – sludge from Drosed.

		1st year	
$LSD_{0.05}$	I cut	II cut	III cut
for fertilization	10.77	13.99	12.329
for soil	5.731	7.440	6.556
for liming	5.731	7.440	6.556
for fertilization x soil	15.24	19.79	17.436
for fertilization x liming	15.24	19.79	17.436
for liming x soil	8.104	ns	ns
		2nd year	
for fertilization	11.19	12.69	ns
for soil	5.949	n.i.	ns
for liming	5.949	6.749	9.336
for fertilization x soil	15.82	17.95	24.83
for fertilization x liming	15.82	17.95	24.83
for liming x soil	8.413	9.545	13.20

Liming decreased only zinc concentration at Italian ryegrass, but the influence on other studied elements was not explicit.

Conclusions

1. Contents of Cu, Zn, and Fe in sewage sludge allowed for its utilization for agricultural purposes.
2. Organic fertilization significantly elevated Cu, Zn, and Fe concentration in Italian ryegrass.
3. Considerably higher copper and iron content were recorded in grass grown on the light soil.
4. Liming significantly decreased Zn content in Italian ryegrass.

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ODDZIAŁYWANIE OSADÓW ŚCIEKOWYCH I WAPNOWANIA NA ZAWARTOŚĆ MIEDZI, CYNKU I ŻELAZA W ŻYCICY WIELOKWIATOWEJ (*Lolium multiflorum* Lam.)

Katedra Gleboznawstwa i Chemii Rolniczej
Uniwersytet Przyrodniczo-Humanistyczny w Siedlcach

Abstrakt: W pracy przedstawiono wyniki badań, których celem było określenie wpływu stosowania osadów ściekowych z dwóch oczyszczalni ścieków na glebę lekką i średnią oraz wapnowania na zawartość Cu, Zn i Fe w życicy wielokwiatowej.

Zawartość tych metali stwierdzona w zastosowanych osadach pozwala na ich wykorzystanie do celów rolniczych. Czynniki badane w doświadczeniu miały duży wpływ na zawartość miedzi, cynku i żelaza w roślinach. Nawożenie osadami ściekowymi powodowało znaczny wzrost zawartości Cu, Zn i Fe w życicy wielokwiatowej. Podobnie gatunek gleby miał duży wpływ na zawartość miedzi i żelaza w roślinach, powodując wzrost ich zawartości w życicy uprawianej na glebie lekkiej. Wapnowanie w sposób niejednoznaczny różnicowało zawartość Cu i Fe w roślinach, ale istotnie obniżyło zawartość Fe w życicy.

Słowa kluczowe: osady ściekowe, miedź, cynk, żelazo, wapnowanie, życica wielokwiatowa (*Lolium multiflorum* Lam.)

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Anna KARCZEWSKA[1], Karolina LEWIŃSKA,
Marta AGATA and Agnieszka KRYSIAK

SOIL POLLUTION BY ARSENIC WITHIN THE ALLOTMENT GARDENS IN ZLOTY STOK

ZANIECZYSZCZENIE ARSENEM GLEB OGRÓDKÓW DZIAŁKOWYCH W ZŁOTYM STOKU

Abstract: The aim of the study was to determine arsenic contents in soils of allotment gardens in the town Zloty Stok, which was formerly the greatest European centre of arsenic industry, as well as to assess ecological risk caused by soil contamination. Two complexes of allotment gardens, where soil samples were collected from the depths of 5–15 cm and 30–40 cm, were investigated.

The soils were rich in organic matter and indicated favourable sorption properties. Total contents of arsenic in soils of both garden complexes were extremely high (with the mean 232 mg $\cdot$ kg^{-1} in the surface layers and 281 mg $\cdot$ kg^{-1} in subsurface layers), and exceeded by manifold the value of Polish soil quality standard established as 20 mg $\cdot$ kg^{-1}. Actually soluble forms of arsenic, determined by extraction with 0.05 mol $\cdot$ dm^{-3} $(NH_4)_2SO_4$, proved to be generally low, ie 2.0 % of total on average. At the same time, potentially soluble arsenic content, mainly adsorbed on organic matter and iron oxides, determined by extraction with 0.05 mol $\cdot$ dm^{-3} $NH_4H_2PO_4$, was relatively high, in the range: 14.0–136 mg $\cdot$ kg^{-1} (with the mean 17.2 % of total As). The results indicate that certain environmental risk exists and allotment gardens in Zloty Stok should be excluded at least from a home production of vegetables and other edible plants.

Keywords: arsenic, solubility, soils, Zloty Stok, allotment gardens

Soil contamination with arsenic does not make, generally, a serious problem in Poland, such as it is in many countries of the world, like in India, China or Chile [1–3], but there are some sites in Poland, where arsenic occurs in the environment, including soils, in high concentrations [4]. Zloty Stok, a former arsenic mining and processing center, belongs to those sites. The town, situated at the foot of Zlote Mountains, has a long history of gold and arsenic mining, which began in the thirteenth century. Arsenic processing started there in the seventeenth century and lasted until 1962. Mining generated large quantities of waste materials, including waste rock and slag, which were disposed in nearby valleys. Soils within the mining area have been polluted by air-borne arsenic. Additionally, numerous mine spoils, slag dumps and tailings

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[1] Institute of Soil Science and Environmental Protection, Wroclaw University of Environmental and Life Sciences, 50–357 Wrocław, ul. Grunwaldzka 53, Poland, phone +48 71 320 5639, email: anna.karczewska@up.wroc.pl

remained in the vicinity of the town, and extremely high concentrations of arsenic in surrounding soils have already been reported [4, 5]. In spite of the fact that environmental pollution in this area has been proved, soil pollution within the town was not closer investigated, and there are no data available on arsenic contents and mobility in soils in home gardens or allotment gardens.

There are two groups of allotment gardens in Zloty Stok, divided into hundreds of parcels cultivated individually, where gardeners not only cultivate grasslands and ornamental plants, but grow vegetable and fruits as well. The risk of arsenic mobilization into groundwater as well as the hazard of its possible plant uptake depends on soil properties, such as pH, contents of iron oxides, organic matter and phosphates, and several other factors including soil redox potential. Environmental risk caused by the presence of arsenic in soils can be assessed by the extraction of its easily soluble forms as well as potentially soluble forms, mainly sorbed specifically by iron hydroxides [5–7].

In this paper, we present the results of the study in which the properties of soils, including total contents of arsenic and its actual and potential solubility were examined in the main complexes of allotment gardens in Zloty Stok. Compared were arsenic contents and soluble forms in the surface and subsurface soil layers, which let us draw some conclusions as to the sources and extent of soil pollution.

Material and methods

Soil samples were collected from two complexes of allotment gardens Radosc and Relaks, situated in the town of Zloty Stok and indicated in the map (Fig. 1). In each

Fig. 1. Location of allotment garden complexes Radosc and Relaks in Zloty Stok [8]

garden complex, the samples were taken in 6 sites, from two soil layers: surface (at the depth 5–15 cm) and subsurface (at the depth 30–40 cm).

Soil samples were air-dried and sieved to 2 mm prior to analysis. Basic soil properties were determined using standard methods [9]. Particle size analysis of the fraction < 2 mm was carried out by a combined sieve and sedimentation technique, using a hydrometer method. Soil pH was measured potentiometrically in a suspension with 1 mol · dm^{-3} KCl (*m/v*: 1/2.5). Organic carbon was determined oxidometrically with potassium dichromate in a hot sulphuric acid. Alkaline cations were extracted using a batch method with 0.5 mol · dm^{-3} NH_4-acetate, and exchangeable acidity was determined in 1.0 mol · dm^{-3} KCl, and on that basis, cation exchange capacity CEC and base saturation BS were calculated.

Total concentrations of arsenic in soil were measured after microwave acid digestion of soil samples in the mixture of concentrated nitric(V) and hydrochloric acids (HNO_3 + HCl, 3 + 1). The method yields results comparable to the standard method with *aqua regia*. After filtering, the digests were analysed for arsenic using ICP-AES method (Varian Instrument). Analytical procedures of total arsenic determination were validated using certified reference materials (Montana soils: SRM 2710 and SRM 2711 that contained 626 and 105 mg · kg^{-1} As, respectively), as well as with internal standards.

Soluble forms of arsenic in soils were determined in simple extractions with two different solutions, optimised according to the method by Wenzel et al [6]. Easily soluble As was extracted with 0.05 mol · dm^{-3} $(NH_4)_2SO_4$ (1:25, 20°C, 4 h), and specifically bound As, believed to reflect potentially soluble pool of these elements was extracted with 0.05 mol · dm^{-3} $NH_4H_2PO_4$, (1:25, 20 °C, 16 h).

Results and discussion

The basic properties of all soils did not show great diversity, and proved to match the typical features of soil cover in that region [4] and those of garden soils. All the data on basic soil properties are presented in Table 1.

Table 1

Basic properties of investigated soils, mean values and ranges

Gardens	Depth [cm]	N	Value	Percentage of grains < 0.02 mm	Percentage of grains < 0.002 mm	Organic C	pH_{KCl}	CEC	BS
				[%]		[%]		[mmol$^{(+)}$ · kg^{-1}]	[%]
Radosc	5–15	6	range	15–44	1–5	2.3–5.1	6.1–7.0	17.7–28.0	87–95
			mean	26	3	3.9	6.6	23.6	92
	30–40	6	range	30–61	2–18	0.1–2.1	5.9–7.0	13.1–21.8	83–95
			mean	43	8	1.3	6.4	18.8	92
Relaks	5–15	6	range	15–26	2–4	4.3–5.6	5.0–7.0	13.5–29.4	76–94
			mean	20	3	4.9	6.2	22.9	87
	30–40	6	range	20–34	0–6	1.2–3.3	5.0–6.6	12.0–21.4	78–93
			mean	29	3	1.8	5.9	16.8	87

Grain size composition of soils, assigned to the textural groups according to USDA [10], was determined as sandy loam, with locally occurring silt loams in the garden complex Radosc. All soil contained low proportion of clay fraction (4 % being the mean value of all samples), and comparable contributions of silt and sand fractions. Soil pH varied in the range of 5.0–7.0, with neutral or slightly acidic reaction in most cases. Higher pH values in the surface soil layers than those in subsurface layer are typical for intensively used and often limed soils, like horticultural soils. High content of organic matter both in surface and subsurface soil layers, are typical for garden soils as well. The soils contained 2.3–5.6 %, and 0.1–3.3 % of organic carbon ($C_{org.}$) in upper and lower soil layers, respectively. High amounts of organic matter went together with beneficial sorption properties. The values of the cation exchange capacity (CEC) were in the ranges 131–294 $mmol^{(+)} \cdot kg^{-1}$ in the upper soil layer and 120–218 $mmol^{(+)} \cdot kg^{-1}$ in the lower one. Generally, the basic properties of soils should be described as beneficial for plant cultivation and amateur garden production.

Closer examination of soil chemistry, in particular contents of arsenic, gives however, quite different assessment. Total concentrations of arsenic were extremely high in all investigated soil samples, and ranged from 72 to 451 $mg \cdot kg^{-1}$ (Table 2). It is worth mentioning, that Polish soil quality standards define the level of 20 $mg \cdot kg^{-1}$ as maximum acceptable arsenic content in soils used for both agricultural or horticultural purposes, as well as for soils in recreational areas [11]. Total arsenic concentrations in subsurface soil layer (74–451 $mg \cdot kg^{-1}$) were higher even than those in surface soil layer (72–303 $mg \cdot kg^{-1}$), though the difference was not statistically significant at p = 0.95. The results characterizing total arsenic in soils of two garden complexes did not significantly differ either. Presumably, air-borne arsenic was not the only source of this element in the soils examined. Such statement may be based on the data on relatively high arsenic concentrations in subsurface soil, matched together with general knowledge on limited mobility of this element in the soil environment [1, 2, 7, 12, 13]. Possible other sources of soil arsenic might have been: 1) either mine water, used there commonly for soil watering and containing high contents of arsenic in easily soluble forms, or 2) high contents inherited in soil parent rock, of either natural or anthropogenic origin. It is also possible, that originally higher arsenic concentrations in the surface soil layer have been "diluted" with foreign material used for cultivation, such as organic fertilizers. Further studies are needed to give better light to the problem of arsenic origin in garden soils.

Table 2

Total content of arsenic [$mg \cdot kg^{-1}$]

Gardens	Depth [cm]	N	Value			
			minimum	maximum	mean	SD
Radosc	5–15	6	72	303	213	85
	30–40	6	74	357	251	114
Relaks	5–15	6	211	272	250	23
	30–40	6	237	451	310	83

At this stage of the study, at least preliminary data were required to estimate the environmental risk caused by arsenic presence in soil and to assess related hazards to human health. Therefore, arsenic solubility in soils was determined, including both actual solubility (easily soluble forms) and potential solubility (the forms specifically bound, mainly to organic matter and iron oxides). Actually soluble forms of arsenic, as determined by extraction with 0.05 mol $\cdot$ dm^{-3} $(NH_4)_2SO_4$, proved to be generally low, in the range 0.7–11.0 mg $\cdot$ kg^{-1}, which corresponded to 0.3–3.5 % (2.0 % on average) of soluble arsenic contributions to its total pools in soils (Table 3).

Table 3

Easily soluble arsenic in soils

Gardens	Depth [cm]	N	Contents [mg · kg^{-1}]			Percent of total As		
			range	mean	SD	range	mean	SD
Radosc	5–15	6	2.5–4.8	3.7	1.2	1.3–3.4	2.5	1.1
	30–40	6	2.6–11.0	6.8	4.2	2.6–3.5	3.1	0.5
Relaks	5–15	6	2.5–3.0	2.8	0.4	1.1–1.2	1.2	0.1
	30–40	6	0.7–9.3	4.3	4.5	0.3–2.1	1.2	0.9

The extent of this study did not allow to find any statistical relationships between soil properties and arsenic solubility, but it should be mentioned that the highest absolute concentrations of easily soluble arsenic were found in the samples collected from the layer 30–40 cm.

The contributions of potentially soluble arsenic, determined by extraction with 0.05 mol $\cdot$ dm^{-3} $NH_4H_2PO_4$, in soils were relatively high (Table 4), in the range: 14–136 mg $\cdot$ kg^{-1} (with the mean value 41.6 mg $\cdot$ kg^{-1}, and average contribution to total As: 17.2 %).

Table 4

Potentially soluble arsenic in soils

Gardens	Depth [cm]	N	Concentrations [mg · kg^{-1}]			Percent of total As		
			range	mean	SD	range	mean	SD
Radosc	5–15	6	14.0–29.3	21.8	7.7	7.5–19.5	14.7	6.3
	30–40	6	22.7–95.3	52.8	37.8	15.0–30.5	24.6	8.4
Relaks	5–15	6	22.8–24.2	23.5	1.0	8.7–11.5	10.1	2.0
	30–40	6	29.8–136	68.4	38.7	11.6–30.1	19.4	6.6

The contents of potentially soluble arsenic were in subsurface layer higher than those in the surface soil, and this difference proved statistically significant at $p = 0.95$. The highest contributions of specifically bound arsenic reached the values of 30 % of total and were found in subsurface soil layer. There were no significant differences between the contributions of potentially soluble arsenic in soils of both garden complexes. Such high contributions of specifically bound arsenic were not found in the other sites in Zloty Stok, affected by arsenic mining and processing activities [4, 5].

The results indicate, that arsenic presence in soils may cause serious environmental risk, as its easily soluble and specifically bound forms may be mobilized, due to strong changes in soil pH, and more likely, because of changing redox conditions [1, 5, 7, 13].

Conclusions

The soils of two main garden complexes in Zloty Stok, both in their surface and subsurface layers, contained extremely high concentrations of arsenic, by manifold exceeding those established as soil quality standards.

The origin of arsenic in those soils should be closer studied, as it may be crucial for predicting further behaviour and mobility of this toxic element.

Actual solubility of arsenic in soils remains relatively low, but the contributions of potentially soluble, specifically bound forms, are high, and when mobilized may cause serious risk of water pollution and increased plant uptake. The factors maintaining the processes of arsenic mobilization and bioavailability in those specific soils, require thorough examination.

To minimize the risk to human health, at least the production of plants for consumption, such as vegetables or fruits in the allotment gardens in Zloty Stok should be definitely banned.

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ZANIECZYSZCZENIE ARSENEM GLEB OGRÓDKÓW DZIAŁKOWYCH W ZŁOTYM STOKU

Instytut Nauk o Glebie i Ochrony Środowiska
Uniwersytet Przyrodniczy we Wrocławiu

Abstrakt: Celem niniejszej pracy było określenie zawartości arsenu w glebach ogródków działkowych Złotego Stoku, niegdyś największego w Europie ośrodka przetwórstwa arsenu, a także ocena zagrożenia ekologicznego wynikającego z zanieczyszczenia gleb tym pierwiastkiem. Badano gleby dwóch zespołów ogrodów, w których pobrano próbki z głębokości 5–15 cm i 30–40 cm.

Gleby wykazywały znaczną zawartość materii organicznej oraz korzystne właściwości sorpcyjne. Całkowita zawartość As w glebach obu kompleksów była bardzo duża (średnio 232 mg $\cdot$ kg^{-1} w warstwie powierzchniowej i 281 mg $\cdot$ kg^{-1} w podpowierzchniowej) i w obu zespołach ogrodów znacznie przekraczała wartość 20 mg $\cdot$ kg^{-1} określoną w Rozporządzeniu Ministra Środowiska jako standard jakości gleby. Udział łatwo rozpuszczalnych form arsenu, określanych na podstawie ekstrakcji roztworem 0,05 mol $\cdot$ dm^{-3} $(NH_4)_2SO_4$, był mały i wynosił średnio 2% całkowitej zawartości arsenu, ale udział form potencjalnie rozpuszczalnych, związanych z substancją organiczną oraz uwodnionymi tlenkami żelaza, ekstrahowanych 0,05 mol $\cdot$ dm^{-3} $NH_4H_2PO_4$, był znaczny, w przedziale: 14.0–136 mg $\cdot$ kg^{-1} (i średnio odpowiadał 17.2 % całkowitej zawartości As w glebach). Uzyskane wyniki wskazują, że istnieje ryzyko środowiskowe związane z zanieczyszczeniem gleb arsenem i dlatego należy ograniczyć użytkowanie gleb ogrodów działkowych w Złotym Stoku, przynajmniej w zakresie produkcji warzyw i innych roślin na cele konsumpcyjne.

Słowa kluczowe: arsen, rozpuszczalność, gleby, Złoty Stok, ogródki działkowe

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Tomasz KLEIBER[1], Maciej BOSIACKI[1]
and Bartosz MARKIEWICZ[1]

EFFECT OF THE CONTROLLED FERTILIZATION ON THE MINERAL COMPONENTS OF CHOSEN VARIETIES OF ONION (*Allium cepa* L.)
PART II. MICROELEMENTS AND SODIUM

WPŁYW KONTROLOWANEGO NAWOŻENIA NA ZAWARTOŚĆ SKŁADNIKÓW POKARMOWYCH W WYBRANYCH ODMIANACH CEBULI (*Allium cepa* L.)
CZ. II. MIKROSKŁADNIKI I SÓD

Abstract: The paper presents results of studies whose objective was the estimation of the controlled fertilization effect and the bulbs storage – in case of chosen cultivars (21) – on the nutritive value of onion defined on the basis of microelements: iron, manganese, zinc and copper and sodium contained in edible parts of onion. During whole of the vegetative studies there were used controlled fertilization based on the chemical analysis of soil. A significant modifying effect of the cultivar was exerted on the content of the majority of the studied components: manganese, copper and sodium in the dry matter of onion. No effect was found to be exerted by the cultivar on the content of iron and zinc. Storage of onion – similarly as the cultivar – significantly modified the content of manganese and copper, but it did not differentiate the content of sodium, zinc and iron. The determined content of microelements ranged [$\text{mg} \cdot \text{kg}^{-1}$ d.m.] for: iron 42.6–96.4 mg Fe; manganese 2.6–11.2 mg Mn; zinc 16.9–27.3 mg Zn; copper 4.61–6.85 mg Cu. The determined contents of sodium ranged from 0.16 to 0.40 % Na in onion dry matter. A comparison of the nutritive value of onion with other vegetable species indicated that onion is a comparatively rich source of microelements and sodium in the human diet. Thanks to controlled fertilization based on regular chemical soil analyses is possible to obtain good nutritive value of crops and protect the soil environment against possible contamination with excessive mineral fertilizers.

Keywords: onion, controlled fertilization, nutritive value, microelements, cultivar-induced differentiation, storage

The group of macroelements required daily by human body in an amount exceeding 100 mg per 1 person includes: nitrogen, phosphorus, calcium, magnesium and potassium, sodium and chlorine [1]. On the other hand, microelements whose daily

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

demand is below 100 mg · person^{-1} include among others: iron, manganese, zinc, copper and iodine. The basic source of the above-mentioned components in human diet are: meat, dairy produce, fruits and vegetables. Therefore, it is important to diversify the daily diet with the most valuable products.

One of the most frequently consumed vegetables in Poland is onion [2]. The objective of the presented studies was the estimation of the effect of controlled fertilization in case of 21 chosen cultivars of onion and the bulb storage on the nutritive value defined on the basis of the content of microelements (iron, manganese, zinc, copper) and sodium contained in onion bulbs. Furthermore, the nutritive value of onion was evaluated in relation to other vegetables like: red paprica [3], common red cabbage [4], carrot [1], cucumbers [5] and cocktail tomatoes [6].

Material and methods

In the years 2008–2009, field and laboratory experiments were carried out aiming at the estimation of the controlled fertilization and storage of bulbs effect in controlled conditions on the microelement composition and sodium content in onion bulbs (in case of 21 chosen cultivars). Vegetation experiments were carried out in a private horticultural farm growing a collection of 83 onion cultivars. Laboratory experiments were performed in the Experimental Station of the Horticultural Department "Marcelin", University of Life Sciences in Poznan. A detailed description of the applied methods is contained in an earlier paper of the authors [7].

The soil before seeds sowing characterized following of average chemical composition (in mg · dm^{-3}): N-NH$_4$ 12.0, N-NO$_3$ 0.0, P-PO$_4$ 49.0, K 75.1, Ca 720.0, Mg 44.1, S-SO$_4$ 0.1, Cl 13.0, Fe 30.6, Mn 4.1, Zn 5.0, Cu 0.1, pH 7.80, EC 0.20 mS · cm^{-1}. The content of nutritive components was maintained based on the cyclical chemical soil analyses on the standard level (in mg · dm^{-3}): N 90.0, P 70.0, K 225.0, Mg 90.0, Fe 50.0, Mn 15.0, Zn 25.0, Cu 5.0, pH in H_2O 6.0–6.5, EC < 0.6 mS · cm^{-1} [8–10 modified]. It was used fertilizers in following doses (per ha): 180 kg of nitrate ammonium (34 % N), 300 kg of double phosphate (40 % P_2O_5), 200 kg of potassium sulphure (50 % K_2O), 150 kg of magnesium sulphure (16 % MgO), 30 kg manganese sulphure (32.3 % Mn), 30 kg zinc sulphure (22 % Zn), 40 kg copper sulphure (25.6 % Cu), 2 kg of borax (11.3 % B).

After the termination of the vegetation period 18–20 onions representative of the given cultivar were collected from the field patches, healthy specimens, without any syndroms of damages or diseases were selected. The collected material was divided into two equal parts. One half of the onions was peeled, sliced, dried at 45–50 ^{o}C and ground. The other half of the collected plant material was transferred for 60 days to a refrigerator (at temperature of 6 ^{o}C and air humidity 50 %) and the further procedure was the same as in case of onion freshly collected.

For the determination of general sodium forms – the plant material was mineralized in concentrated sulfuric acid, while iron, manganese, zinc and copper were mineralized in a mixture of nitric(V) and chloric(VII) acids (3:1 v/v); [11]. After mineralization of the plant material, the following determinations were performed: Fe, Mn, Zn, Cu, Na –

by AAS method (on Carl Zeiss Jena apparatus). Statistical analysis of the results of component contents in onion bulbs was carried out. Conclusions were drawn at significance level of $\alpha = 0.05$.

Results and discussion

Effect of the cultivar on the content of microelements and sodium

A significant influence of the studied cultivar types was found to be exerted on the content of manganese, copper and sodium in the dry matter of onion (Tables 1, 2).

Table 1

Effect of cultivar and of the storage on the content of iron and manganese [mg · kg^{-1} d.m.] and on the coefficient of variation

Variety (A)	Fe			Mn		
	T1(B)	T2(B)	Mean	T1(B)	T2(B)	Mean
‘Aurora’	54.6	70.1	62.4	3.4	6.0	4.7
‘Bennito’	57.2	59.3	58.2	5.0	8.2	6.6
‘Consuelo’	65.3	70.8	68.1	4.5	5.1	4.8
‘Cymes’	45.7	61.2	53.4	2.5	4.6	3.6
‘Eureka’	54.3	49.9	52.1	4.4	4.9	4.7
‘Grabowska’	69.7	73.5	71.6	8.1	14.3	11.2
‘Kutnowska’	51.2	53.3	52.2	2.5	5.1	3.8
‘Lawica’	59.5	60.2	59.9	4.9	11.8	8.3
‘Marbella’	109.0	83.8	96.4	3.4	4.4	3.9
‘Mission’	55.9	62.1	59.0	4.2	9.9	7.1
‘Napoleon’	65.1	54.6	59.8	2.8	4.1	3.5
‘Sherpa’	67.7	70.0	68.9	2.6	4.0	3.3
‘Slawa Ozarowa’	59.9	67.9	63.9	2.4	5.9	4.1
‘Sochaczewska’	67.8	57.0	62.4	3.4	9.0	6.2
‘Stamford’	69.5	74.3	71.9	4.6	5.6	5.1
‘Tandem’	73.9	54.6	64.3	2.4	3.5	2.9
‘Topolska’	49.6	51.0	50.3	4.4	10.6	7.5
‘Wiktoria Skierniewicka’	52.6	64.6	58.6	2.2	3.0	2.6
‘Wojka’	38.9	57.8	48.4	2.8	7.5	5.2
‘Wola’	53.3	54.4	53.8	3.1	3.3	3.2
‘Wolska’	40.7	44.6	42.6	1.8	4.0	2.9
Mean	60.1	61.7	60.9	3.6	6.4	5.0
CV [%]	76.1	28.1	57.7	39.2	47.9	55.5
LSD for A		ns			2.83	
LSD for B		ns			0.46	
LSD for A×B		ns			0.96	

T1 – directly after harvest; T2 – after 60 days of storage; ns – no significant.

However, cultivar did not differentiate significantly the content of iron and zinc. Iron contents determined in the studies ranged from 42.6 mg Fe (cv. ‘Wolska’) to 96.4 mg Fe · kg^{-1} (cv. ‘Marbella’). However, for the majority of cultivars, iron contents ranged from 50 to 60 mg Fe. The mean iron value in onion was 65.2 mg Fe · kg^{-1}. The cv. ‘Wiktoria Skierniewicka’ was characterized by a significantly smallest content of manganese (2.6 mg Mn · kg^{-1}), while ‘Grabowska’ cultivar showed the highest value of this component (11.2 mg Mn · kg^{-1}) with a mean content equal to 5.0 mg Mn · kg^{-1}. Content of zinc ranged from 16.9 mg Zn · kg^{-1} (cv. ‘Wolska’) to 27.3 mg Zn · kg^{-1} (cv. ‘Bennito’) (Table 2).

Table 2

Effect of cultivar type and of the storage on the content of zinc, copper [mg · kg^{-1} d.m.] and sodium [% d.m.] and the coefficient of their variation

Variety (A)	Zn			Cu			Na		
	T1(B)	T2(B)	Mean	T1(B)	T2(B)	Mean	T1(B)	T2(B)	Mean
‘Aurora’	19.6	23.4	21.5	7.41	5.79	6.60	0.20	0.26	0.23
‘Bennito’	27.2	27.4	27.3	7.62	6.08	6.85	0.30	0.20	0.25
‘Consuelo’	23.7	24.1	23.9	5.90	6.18	6.04	0.30	0.26	0.28
‘Cymes’	17.8	17.6	17.7	7.51	4.63	6.07	0.20	0.26	0.23
‘Eureka’	22.6	23.4	23.0	6.17	5.32	5.75	0.30	0.27	0.29
‘Grabowska’	25.7	29.9	27.8	6.37	7.31	6.84	0.20	0.11	0.16
‘Kutnowska’	18.1	16.2	17.2	5.34	4.99	5.16	0.20	0.17	0.19
‘Lawica’	16.5	20.0	18.3	6.50	5.55	6.02	0.20	0.20	0.20
‘Marbella’	20.3	20.5	20.4	6.19	5.80	6.00	0.20	0.20	0.20
‘Mission’	23.1	26.1	24.6	5.88	5.75	5.82	0.20	0.19	0.20
‘Napoleon’	20.4	20.8	20.6	6.75	5.68	6.22	0.20	0.20	0.20
‘Sherpa’	20.4	21.6	21.0	4.93	4.29	4.61	0.30	0.16	0.23
‘Slawa Ozarowa’	18.1	22.8	20.5	5.82	4.76	5.29	0.20	0.19	0.20
‘Sochaczewska’	22.0	24.6	23.3	5.71	4.65	5.18	0.20	0.26	0.23
‘Stamford’	26.2	22.2	24.2	6.29	4.74	5.52	0.20	0.20	0.20
‘Tandem’	16.4	20.7	18.6	6.06	5.79	5.93	0.30	0.18	0.24
‘Topolska’	19.6	25.4	22.5	5.20	6.15	5.68	0.20	0.26	0.23
‘Wiktoria Skierniewicka’	16.5	17.6	17.1	5.88	4.99	5.44	0.30	0.50	0.40
‘Wojka’	16.7	20.9	18.8	5.71	6.47	6.09	0.20	0.26	0.23
‘Wola’	18.5	20.8	19.7	5.77	5.86	5.82	0.20	0.26	0.23
‘Wolska’	15.5	18.2	16.9	5.71	5.54	5.63	0.20	0.26	0.23
Mean	20.2	22.1	21.2	6.13	5.54	5.8	0.23	0.23	0.23
CV [%]	123.7	15.4	91.5	11.9	13.8	13.7	23.0	54.1	105.5
LSD for A	ns			0.59			0.15		
LSD for B	ns			0.60			ns		
LSD for A×B	ns			0.57			0.02		

Descriptions as in Table 1.

Mean value from all studied cultivars was 23.1 mg Zn · kg^{-1}. ‘Sherpa’ was a cultivar with the significantly smallest content of copper (4.61 mg Cu · kg^{-1}), while ‘Bennito’ cultivar showed the highest Cu content (6.85 mg Cu · kg^{-1}). The determined contents of sodium ranged from 0.16 % (in case of cv. ‘Grabowska’) to 0.40 % Na (for cv. ‘Wiktoria Skierniewicka’). Cultivar type exerted a significant influence on the content of the studied components. Mean coefficients of variation in the content of the studied components were distinctly higher than in case of macroelements [7], ranging from 13.7 % (in case of copper) to 105.5 % (in case of sodium).

Effect of onion storage on the content of microelements and sodium

Storage exerted a significant effect on the content of manganese and copper in onion bulbs, but it did not differentiate sodium, zinc and iron. In case of manganese, a significant increase of this component was found (from 3.6 mg Mn · kg^{-1} to 6.4 mg Mn · kg^{-1}). In turn, in case of copper, there was a significant decrease of its content (from 6.1 mg Cu · kg^{-1} to 5.5 mg Cu · kg^{-1}).

Nutritive value of onion against other vegetable species

Estimation of the nutritive value of onion as a species regarding its content of microelements and sodium was carried out by the comparison of the contents determined in our own studies with the contents shown by studies referring to carrot [1], red paprica [3], common red cabbage [4], cucumbers [5], cocktail tomato [6], celery [12], as well as with earlier studies referring to onion [13] (Table 3).

Table 3

Contents of iron, manganese, zinc and copper [mg · kg^{-1} d.m.] and sodium [% d.m.] in the edible part of selected vegetable species (acc. to different authors)

Species	Nutrient				
	Fe	Mn	Zn	Cu	Na
	[mg · kg^{-1} d.m.]				[% d.m.]
Onion – own studies	42.6–96.4	2.6–11.2	16.9–27.3	4.61–6.85	0.16–0.40
Onion	41.8	9.98	26.02	6.02	—
Red paprica	2.2–4.6	0.3–0.8	1.0–2.3	0.3–1.3	—
Common red cabbage	93.4–173.8	25.0–31.4	33.2–39.5	6.4–11.8	—
Carrot	20.0	8.0	23.0	10	0.8
Cucumber	314.03	—	—	23.10	—
Cocktail tomatoes	128.0	—	18.1	—	—
Celery	19.0–105.3	2.1–8.9	12.9–64.6	2.1–8.9	

On the basis of our present studies, one can conclude that onion is a comparatively rich source of microelements and sodium in human diets. The mean value of iron (from the studied cultivars) was similar to the values determined in the earlier studies of this species [13]. Paprica is a less rich source of iron [3]. Celery shows iron value similar to onion [12]. On the other hand, cucumbers and cocktail tomato are characterized by a distinctly higher iron content [6, 5]. Regarding the content of manganese, onion is placed after common red cabbage and cucumber [4, 5], however, its iron content is richer than that represented by paprica [3], but its iron value is similar to that represented by celery [12]. Our determinations of zinc content are similar to the contents reported earlier for onion [13] and tomato [6]. Red cabbage [4] and celery [12] show more zinc than it was found in onion, but paprica is significantly poorer as far as zinc is concerned [3]. Similarly as in case of the remaining microelements, the richest sources of copper are represented by common red cabbage [4], cucumber [5], celery [12] and carrot [1].

Conclusions

1. The cultivar and storage significantly modified the content of manganese, copper and sodium in the dry matter of onion.
2. The studied factors did not differentiated the contents of iron and zinc.
3. During storage time of bulbs there were analyzed, the increase of the content of manganese and sodium in onion dry matter and a decrease of copper was found.
4. A comparison of the nutritive value of onion with other vegetable species indicated that onion is a comparatively rich source of microelements and sodium in the human diet.
5. The controlled fertilization based on regular chemical soil analyses is useful to obtain good micronutritive value of onion crops and protection the soil environment against possible contamination with excessive mineral fertilizers.

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WPŁYW KONTROLOWANEGO NAWOŻENIA NA ZAWARTOŚĆ SKŁADNIKÓW POKARMOWYCH W WYBRANYCH ODMIANACH CEBULI (*Allium cepa* L.)
CZ. II. MIKROSKŁADNIKI I SÓD

Katedra Nawożenia Roślin Ogrodniczych
Uniwersytet Przyrodniczy w Poznaniu

Abstrakt: Przedstawiono wyniki badań, których celem była ocena wpływu kontrolowanego nawożenia i przechowania cebul – w przypadku 21 wybranych odmian – na wartość odżywczą cebuli, określoną na podstawie zawartość w niej mikroelementów: żelaza, manganu, cynku i miedzi oraz sodu zawartych w jadalnych częściach cebuli. W trakcie badań wegetacyjnych stosowano nawożenia kontrolowane za pomocą analiz chemicznych gleby. Wykazano istotny, modyfikujący wpływ odmiany na zawartość większości badanych składników: manganu, miedzi i sodu w suchej masie cebuli. Nie stwierdzono z kolei wpływu odmiany na zawartość żelaza i cynku. Przechowywanie cebuli – podobnie jak odmiana – znacznie modyfikowało zawartość manganu i miedzi – a nie różnicowało z kolei zawartości sodu, cynku i żelaza. Oznaczone w przeprowadzonych badaniach zawartości mikroelementów zmieniały się w zakresie [mg · kg^{-1} s.m.] dla: żelaza 42,6–96,4 mg Fe, manganu 2,6–11,2 mg Mn, cynku 16,9–27,3 mg Zn, miedzi 4,61–6,85 mg Cu. Z kolei oznaczone zawartości sodu mieściły się w zakresie od 0,16 % do 0,40 % suchej masy cebul. Porównanie wartości odżywczej cebuli z innymi gatunkami warzyw wskazuje, że cebula jest bogatym źródłem mikroelementów i sodu w diecie człowieka. Dzięki nawożeniu kontrolowanemu poprzez regularne analizy chemiczne gleby, możliwe jest osiągnięcie plonu o dobrej jakości dietetycznej oraz ochrona środowiska glebowego przed skażeniem nadmiernymi dawkami nawozów mineralnych.

Słowa kluczowe: cebula, kontrolowane nawożenie, wartość odżywcza, mikroelementy, zróżnicowanie odmianowe, przechowywanie

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Agnieszka KLIMKOWICZ-PAWLAS[1]
and Barbara MALISZEWSKA-KORDYBACH

NITRIFICATION POTENTIAL AS INDICATOR OF PAHs ECOTOXICITY IN FRESHLY CONTAMINATED SOILS. EXAMPLE OF PHENANTHRENE AND PYRENE

POTENCJAŁ NITRYFIKACJI JAKO WSKAŹNIK EKOTOKSYCZNOŚCI WWA W GLEBACH ŚWIEŻO ZANIECZYSZCZONYCH. NA PRZYKŁADZIE FENANTRENU I PIRENU

Abstract: The objective of the study was to evaluate the possibility of application of nitrification potential as an indicator of the ecotoxicity of PAHs to soil microorganisms in freshly contaminated soils. The effects of two model PAHs compounds phenanthrene and pyrene were studied under laboratory conditions (incubation of soils for 7 days at 20 ± 2 °C). Eight soil materials originated from ploughing layer (0–20 cm) of soils not exposed to direct PAH sources were applied. Soil materials were spiked with phenanthrene or pyrene at the levels of 1, 10, 100 and 500 mg · kg^{-1}. Contamination of soils with PAHs inhibited the activity of nitrifying bacteria, which appeared to be a sensitive indicator of the presence of PAHs. The effect of hydrocarbons was related to the soil characteristic and compound properties; the strongest inhibition corresponded to light soils with low organic matter content and low biological activity contaminated with phenanthrene, characterized by high water solubility and bioavailability. The high acidity of soils created additional stress to nitrifying bacteria and thus increased their susceptibility to the effect of contaminants such as PAHs.

Keywords: nitrification potential, polycyclic aromatic hydrocarbons, phenanthrene, pyrene, ecotoxicity parameters

There is an increasing interest in developing indicators for evaluation of soil quality, to protect effectively soil habitat function. Soils from agricultural land are often exposed to the influence of stressors such as chemical contaminants. Although parameters describing general microbial activity (eg respiration, total biomass) are not considered to be the good indicators of soil pollution, there are some specific groups of soil microorganisms exhibiting high sensitivity to organic contaminants like PAHs [1–3].

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[1] Department of Soil Science Erosion and Land Conservation, Institute of Soil Science and Plant Cultivation – National Research Institute, ul. Czartoryskich 8, 24–100 Puławy, Poland, email: agnes@iung.pulawy.pl

The good example are nitrifying bacteria playing important role in the cycling of nitrogen in soil environment. They are very sensitive to low concentration of contaminants and rapidly response to soil perturbation [4–6].

Polycyclic aromatic hydrocarbons (PAHs) represent the group of persistent organic pollutants (POPs). Some of them are resistant to physical, chemical and biological degradation and can remain in the environment for a long time [3, 7]. PAHs originate from incomplete combustion or pyrolysis of organic substances like coal, oil, petrol, etc. The other sources of PAHs to soil are disposal of waste materials, creosote use and road runoffs, accidental fuel spills and leakages as well as industrial wastewaters, sewage sludge and compost applied to agricultural land [8, 9]. PAHs incorporated into soil may undergo several processes. The main mechanisms include biodegradation, chemical transformation, volatilization, photolysis, sorption to the soil solid phase, leaching and transfer to plants and grazing animals [3, 8, 10]. PAHs compounds are generally hydrophobic and non-volatile, but individual hydrocarbons exhibit different physicochemical properties, which control their fate, reactivity and effects on soil ecosystems [10, 11].

The main objective of this study was to evaluate the possibility of application of nitrification potential as an indicator of the ecotoxicity of PAHs to soil microorganisms in freshly contaminated soils. Phenanthrene (Phen) and pyrene (Pyr) – the compounds exhibiting high ecotoxic activity [1, 12–14] and being abundant in the soil environment [9] were chosen as model PAHs. The particular attention was paid to soil properties regulating nitrifying bacteria activity and PAHs bioavailability [6, 10, 15].

Materials and methods

Soils characteristic

Eight different soils were used in the laboratory experiments. All soil samples were collected from the typical rural areas (Lublin province, Poland) not exposed to direct PAH sources, from 0–20 cm layer. After transport to the laboratory, soil material was air dried at 20 ^{o}C, well mixed, sieved to pass a 2 mm sieve-mesh and stored for no longer than 6 months in the dark (12–16 ^{o}C) before soil physicochemical characteristic and ecotoxicity testing.

Soil characteristics included the determination of particle size distribution, soil organic carbon content, pH and content of PAHs. Soil particle size distribution was established by an aerometric method [16]. Soil organic carbon (C_{org}) content was determined by sulfochromic oxidation of organic carbon followed by titration of the excess $K_2Cr_2O_7$ with $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ [17]. The pH was measured potentiometrically in 1:2.5 (m/V) suspension of soil in 1 $mol \cdot dm^{-3}$ KCl solution [18].

Thirteen PAH (Σ13PAH) compounds (US EPA list) were determined by extraction with dichloromethane in Soxtec apparatus (Büchi Universal Extraction System B-811) for 6 h. The extracts were concentrated to a volume of 1 cm^3 under vacuum on a rotary evaporator and cleaned up on glass minicolumns (0.5 × 20 cm) filled with 1 g of silica gel (conditioned at 135 ^{o}C for 16 h) suspended in dichloromethane. PAHs were eluted with 5 cm^3 of a mixture of CH_2Cl_2/*n*-heksane (2:3 v/v). The eluate was evaporated to a volume of approximately 1 cm^3 and analyzed on GCQ MAT Finigan gas chromatograph equipped with MS detector with ion trap. Resolution of PAH compounds has been achieved with DB-5 MS fused-silica capillary column 30 m × 0.25 mm I.D. with a film thickness of 0.25 μm and with 10 m guarded column (J&W Scientific, USA). Helium was used as a carrier gas (constant flow of 40 $cm \cdot s^{-1}$) with a splitless injection system at 250 ^oC. The GC oven was programmed as follows: 35 ^oC for 2 min, followed by a 30 $^oC\ min^{-1}$ ramp to 120 ^oC and then with ramp of 5 $^oC\ min^{-1}$ to final temperature of 290 ^oC (10 min hold). Mass spectrometer (MS) detection was based on selected ion monitoring (SIM) system. The solvent blank sample was carried out through all procedures. Quality control included analysis of a reference soil sample (soil No. 701 from SETOC program, 1992–1995) every 20 samples. The precision of the method corresponding to the mean relative standard deviation (RSD) was in the range of 2 to 24 % for individual PAH compounds and 8 % for the sum of 13 PAH compounds. The mean recovery calculated for 13 PAHs in the reference soil was 71 %, with recovery for individual compounds ranged from 53 % for benzo[b]fluoranthene to 112 % for phenanthrene.

PAH characteristic

Two PAH compounds, differing substantially with their physicochemical properties, were used in the studies. 3-ring phenanthrene (M_w = 178) has high water solubility = = 1300 $\mu g \cdot dm^{-3}$, log K_{ow} = 4.57 and Henry's constant = 3.24 $Pa \cdot m^3 \cdot mol^{-1}$, while 4-ring pyrene ($M_w$ = 202) has water solubility = 132 $\mu g \cdot dm^{-3}$, log K_{ow} = 5.18 and and Henry's constant = 0.92 $Pa \cdot m^3 \cdot mol^{-1}$ [11]. Water/organic carbon partition coefficients (K_{oc}), describing sorption affinity of PAHs to soil organic matter, corresponded to 19055 $dm^3 \cdot kg^{-1}$ and 45709 $dm^3 \cdot kg^{-1}$ for phenanthrene and pyrene, respectively [19].

The stock solutions of hydrocarbons were prepared by dissolving 25 g of Phen and Pyr in 1000 cm^3 dichloromethane, stored in the dark at room temperature and diluted further with CH_2Cl_2 according to needs.

Four levels of two PAHs were applied:

I) 1 $mg \cdot kg^{-1}$, corresponding to Σ9PAHs threshold value for agricultural soils according Polish [20] and Dutch regulations [21] and corresponding to Danish ecotoxicological criterion for PAHs in soil [22];

II) 10 $mg \cdot kg^{-1}$, corresponding to German guideline value for soil with respect to the growth and quality of plants [23, 24];

III) 100 $mg \cdot kg^{-1}$, corresponding to German guideline value for soil in industrial areas [24];

IV) 500 $mg \cdot kg^{-1}$, corresponding to PAHs action level according the UK regulations [23].

Experimental procedure

The soils subsamples (100 ± 0.1 g) were placed in glass beakers and spiked with 2 cm^3 of dichloromethane solution of phenanthrene and pyrene at the levels of: 1, 10, 100 and 500 mg of each hydrocarbon *per* kg of dry soil. Each soil sample, after careful mixing with appropriate amount of Phen-CH_2Cl_2 or Pyr-CH_2Cl_2 solution, was left overnight to let the solvent evaporate. After 24 hours the subsamples were supplemented with 200 ± 0.1 g of soil, thoroughly mixed, moistened with deionized water to 55 % water holding capacity and incubated in the dark for 7 days at 20 ± 2 ^{o}C. Soil moisture content was kept at the constant level by periodically weighing the samples and adding water as necessary. Non-spiked soil samples amended with pure dichloromethane (at the amount corresponding to those used in PAH-spiked soils) were applied as a control (zero treatment). Each treatment was replicated two times. After 7 days the soils were mixed and two subsamples (25 ± 0.1 g wet weight) were taken from the each replicate for nitrification potential determinations.

Determination of soil nitrifying bacteria activity

Nitrification potential in soil was determined according to ISO 15685 [25] method. Moist soil subsamples (25 ± 0.1 g) were placed in a 250 cm^3 glass flask and mixed with the mineral medium to form slurry. The volume of medium was calculated by subtracting the volume of water in the initial soil sample from the desired liquid volume 100 cm^3. The mineral medium contained 1.5 mmol · dm^{-3} of diammonium sulphate $(NH_4)_2SO_4$ as a substrate, 1 mmol · dm^{-3} of potassium phosphate buffer (KH_2PO_4 and K_2HPO_4) and 5.625 mmol · dm^{-3} of sodium chlorate(V) (to prevent further oxidation of NO_2^- to NO_3^-). The pH of the medium was approximately 7.2. The soil slurries were mixed for 6 hours on a shaker at approximately 175 rpm at room temperature 20 ± 2 ^{o}C. After incubation 2 cm^3 of the slurry were placed in 25-cm^3 glass beakers and 2 cm^3 of 4 mol · dm^{-3} KCl were added to stop the ammonium oxidation. The suspension was filtered using 390-grade filter paper. Then, 1 cm^3 of the filtrate was transferred to glass flask filled with 20 cm^3 of deionised water and 0.2 cm^3 of the colour reagent containing sulphanilamide ($C_6H_8N_2O_2S$) and *N*-(1-naphtyl)ethylene diamine dihydrochloride ($C_{12}H_{16}N_2Cl_2$). After 60 min, the intensity of the purple colour was measured on Beckman DU-68 spectrophotometer at $\lambda = 543$ nm. In each series of measurements the control samples without soil material were applied. All determinations were done in duplicates for each of the replicate soil samples and the results for individual samples were expressed as an arithmetic mean (μg NO_2^- · g^{-1}) of two measurements adjusted to soil dry matter (105 ^{o}C). The final results were given as an arithmetic mean of four measurements (2 replicates × 2 NP determinations). For ANOVA evaluations, the mean values for the each of the replicates (n = 2) were used.

Precision of the method (corresponding to the RSD values for n = 10) was about 5–8 % for one soil sample and 5–15 % for the replicates of 10 samples (n = 20).

Statistics

To enable comparison of the data for different soils, the results of NP determinations were related to the control (100 %) and expressed as relative nitrification potential (RNP). The analysis of variance method (one-way ANOVA, Tukey HSD test) was applied for the statistical evaluation of the effects. Before ANOVA was performed, the variance check (Bartlett's test appropriate for equal and unequal group size) was done to examine if the samples were from the same populations. Pearson product moment correlations were used for evaluation of relationship between each pair of variables. Normality of all data was checked using standardized skewness and standardized kurtosis parameters.

The ecotoxicity parameters were evaluated on the basis of the determination of the effects of these contaminants on soil microorganisms. The ecotoxic effects of PAHs were expressed as NOEC (*No Observed Effect Concentration*), LOEC (*Lowest Observed Effect Concentration*), EC_{20} and EC_{50} (concentration of Phen or Pyr in soil causing 20 % and 50 % inhibition of NP, respectively). LOEC is the lowest tested concentration that results in a statistically significant adverse effect (in relation to the control). The NOEC is defined as the highest test concentration below the LOEC. EC_{20} and EC_{50} values were calculated on the basis of the best-fit simple regression models (concentration – effect relationship). Statistical evaluations were done using Statgraphics Centurion version XV program.

Results

The applied soils differed in their characteristics, although the range of their properties was not very wide – Table 1. Three soils (No 3–No 5) represented sands, three another (No 6–No 8) – loams, and two soils (No 11–No 12) represented silts. As regards physicochemical properties, the highest variability (CV of 63–77 %) corresponded to the fraction < 0.002 mm and C_{org} contents, while biological activity, expressed by the NP values, differed over one order of magnitude (0.26–5.76 μg $NO_2^- \cdot g^{-1}$). The content of Σ13PAHs in soils was consistently low, much below the limit values set by Polish regulations for the top layer of agricultural soils; the exception was soil No 11, where the concentration of phenanthrene exceeded the limit value of 100 $\mu g \cdot kg^{-1}$ [20]. Generally, the soils exhibited properties typical for Polish agricultural land; they were slightly acidic, with low organic matter content and low level of contamination with PAHs [9, 26].

Amendments of the soils with Phen at the lowest applied level (1 $mg \cdot kg^{-1}$) caused statistically significant inhibition of nitrification potential in four soils (No 3, No 6, No 8 and No 12 – Table 2) with the strongest effect in soil No 3 (RNP of 63 %). The effect increased at the next Phen dose (10 $mg \cdot kg^{-1}$). At the level of 500 mg Phen $\cdot kg^{-1}$ nitrification potential was significantly inhibited in all eight soils, however, high differences between the soils were visible; while RNP in soil No 8 decreased to 75 %, in soil No 11 it was as low as 4 %.

Application of pyrene at the level of 1 $mg \cdot kg^{-1}$ inhibited NP in 6 from 8 tested soils (RNP of 44–91 %) with the exception of soils No 8 and No 12, where the first statistically significant effects were observed at the level 10 and 100 $mg \cdot kg^{-1}$, respectively (Table 2). Increase of the pyrene level to 500 $mg \cdot kg^{-1}$ caused further decrease of microbial activity (in soil No 3 the nitrification potential was totally inhibited).

Table 1

Basic properties of soil materials (n = 8)

Properties / Texture	Soil code								Statistical parameters		
	No 3	No 4	No 5	No 6	No 7	No 8	No 11	No 12	Mean	SD	CV
	Light loamy sand	Light loamy sand	Heavy loamy sand	Sandy loam	Clay loam	Medium loam	Silty loam	Silty clay loam			
fr. < 0.02	15	14	20	29	33	46	35	49	30	13	44
fr. < 0.002	5	3	8	13	14	32	6	15	12	9	77
C_{org}	7.2	6.3	7.0	16.8	15.4	15.3	9.2	32.1	13.7	8.6	63
pH_{KCl}	5.5	5.4	6.4	6.6	7.0	6.9	5.8	7.0	6.3	0.7	11
C:N	7.2	9.0	10.0	14.2	15.4	13.4	8.4	13.4	11.4	3.1	27
NP_{init}	0.39	0.94	0.80	5.76	2.99	4.27	0.26	3.37	2.35	2.05	87
$Phen_{init}$	28	46	15	48	75	43	144	34	54	40	74
Pyr_{init}	20	23	48	22	36	15	16	21	25	11	45
Σ13PAH	303	427	452	477	460	274	377	378	393	74	19

Texture – classification of textural groups according to Polish standard PN-R-04033; fraction content < 0.02 and < 0.002 mm [%]; C_{org} – organic carbon content [$g \cdot kg^{-1}$]; NP_{init} – nitrification potential at the beginning of the experiment [$\mu g\ NO_2^- \cdot g^{-1}$]; $Phen_{init}$ – initial content of phenathrene [$\mu g \cdot kg^{-1}$]; Pyr_{init} – initial content of pyrene [$\mu g \cdot kg^{-1}$]; Σ13PAH – content of 13 PAHs according to US EPA list [$\mu g \cdot kg^{-1}$]; CV – coefficient of variation [%].

Table 2

The results of nitrification potential (NP) determinations in soils contaminated with phenanthrene and pyrene (range 0–500 mg · kg^{-1}) after 7 days of incubation. The values are means for two replications (n = 2) ± SD

PAH level[1]	NP* [µg NO_2^- · g^{-1}]							
	No 3	No 4	No 5	No 6	No 7	No 8	No 11	No 12
Phenanthrene								
Control 0	0.43 ± 0.04^{a}	0.99 ± 0.04^{a}	0.67 ± 0.02^{a}	4.62 ± 0.21^{a}	2.66 ± 0.16^{a}	3.04 ± 0.15^{a}	0.13 ± 0.01^{a}	1.90 ± 0.07^{a}
1	0.27 ± 0.02^{b}	0.98 ± 0.05^{a}	0.66 ± 0.05^{a}	4.17 ± 0.16^{b}	2.70 ± 0.08^{a}	2.80 ± 0.08^{b}	0.13 ± 0.01^{a}	1.73 ± 0.07^{b}
10	0.25 ± 0.03^{b}	0.97 ± 0.04^{a}	0.52 ± 0.02^{b}	3.90 ± 0.20^{b}	2.54 ± 0.08^{a}	2.72 ± 0.12^{b}	0.04 ± 0.01^{b}	1.70 ± 0.04^{b}
100	0.09 ± 0.02^{c}	0.73 ± 0.04^{b}	0.24 ± 0.02^{c}	3.01 ± 0.17^{c}	1.99 ± 0.08^{b}	2.70 ± 0.15^{b}	0.02 ± 0.00^{c}	1.42 ± 0.08^{c}
500	0.04 ± 0.00^{c}	0.61 ± 0.02^{c}	0.15 ± 0.02^{c}	2.63 ± 0.17^{c}	1.11 ± 0.07^{c}	2.27 ± 0.20^{c}	0.01 ± 0.00^{d}	1.08 ± 0.05^{d}
Pyrene								
Control 0	0.15 ± 0.02^{a}	0.87 ± 0.05^{a}	0.63 ± 0.02^{a}	3.44 ± 0.20^{a}	1.96 ± 0.02^{a}	2.92 ± 0.01^{a}	0.09 ± 0.02^{a}	1.72 ± 0.08^{a}
1	0.10 ± 0.02^{b}	0.74 ± 0.02^{b}	0.53 ± 0.02^{b}	3.12 ± 0.07^{b}	2.32 ± 0.02^{b}	2.84 ± 0.07^{a}	0.04 ± 0.01^{b}	1.70 ± 0.14^{a}
10	0.09 ± 0.02^{b}	0.59 ± 0.02^{c}	0.58 ± 0.01^{c}	3.25 ± 0.25^{b}	2.36 ± 0.03^{b}	2.72 ± 0.05^{b}	0.04 ± 0.01^{b}	1.66 ± 0.02^{a}
100	0.04 ± 0.01^{c}	0.48 ± 0.02^{d}	0.53 ± 0.02^{b}	2.83 ± 0.08^{c}	1.96 ± 0.02^{a}	2.57 ± 0.05^{c}	0.02 ± 0.00^{c}	1.60 ± 0.02^{b}
500	0.00 ± 0.00^{d}	0.40 ± 0.02^{e}	0.54 ± 0.08^{b}	2.76 ± 0.08^{c}	1.96 ± 0.02^{a}	1.81 ± 0.07^{d}	0.01 ± 0.00^{d}	1.52 ± 0.02^{c}

[1] Level of PAH [mg · kg^{-1}]; * NP – nitrification potential. The values in columns followed by the same letter are not significantly different (one-way ANOVA, Tukey HSD test) at $p \leq 0.05$ level.

In 15 % of soils the lower levels of contamination (1 and 10 mg · kg^{-1}) led to stimulation of NP activity. Stimulatory effects were most distinct in soil No 7 contaminated with pyrene (Table 2).

Toxic activity of PAHs on nitrification potential was related to PAH properties. The comparison of the reaction of nitrifying bacteria in soils contaminated with phenanthrene and pyrene at the level of 100 and 500 mg · kg^{-1} is presented in Fig. 1. In most of the cases (60 % of soils), stronger effects were observed for Phen than for Pyr.

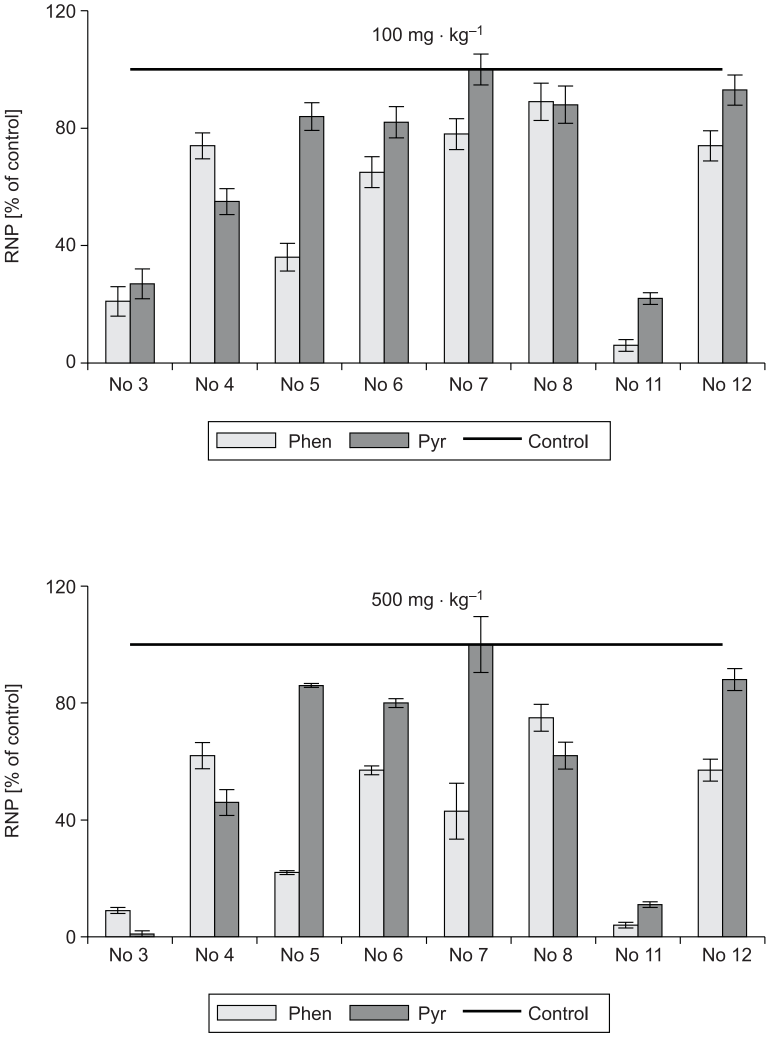


Fig. 1. Comparison of the relative nitrification potential RNP (expressed as a percent of control; control = 100 %) in soils contaminated with phenanthrene and pyrene at the levels of 100 and 500 mg · kg^{-1}. Bars represent 95 % Tukey HSD intervals

Property of soil was the other factor affecting reaction of nitrification bacteria to contamination with PAHs – Table 2. Nevertheless, the correlation coefficients (r) between soil parameters and the effects of PAHs on NP were rather low and significant mainly for pyrene – Table 3. The highest r values for Pyr corresponded to soil acidity (for pH_{KCl} r = 0.63), to C:N ratio (r = 0.65) and to initial nitrification activity of soils (r = 0.49). The correlation between PAHs effect and soil properties was more distinct at the higher doses of PAHs – 100 and 500 mg · kg^{-1}. For further evaluation of those effects the soils were divided into two groups. The first one (soils No 3, No 4, No 5 and No 11) represented low C_{org} contents (< 9.2 g · kg^{-1}), pH values < 6.4 and low microbial activity (NP < 0.94 μg NO_2^- · g^{-1}). The second group of soils (No 6, No 7, No 8 and No 12) had organic carbon content in the limits of 15.3–32.1 g · kg^{-1}, neutral pH (6.6–7.0) and higher values of NP (2.99–5.76 μg NO_2^- · g^{-1}). The significant differences in reaction of microorganisms in both groups of soils were visible at the levels > 100 mg · kg^{-1} (Fig. 2). Both phenanthrene and pyrene exhibited stronger toxic activity in light soils from group I, where RNP values were about 30 % lower than in the group II.

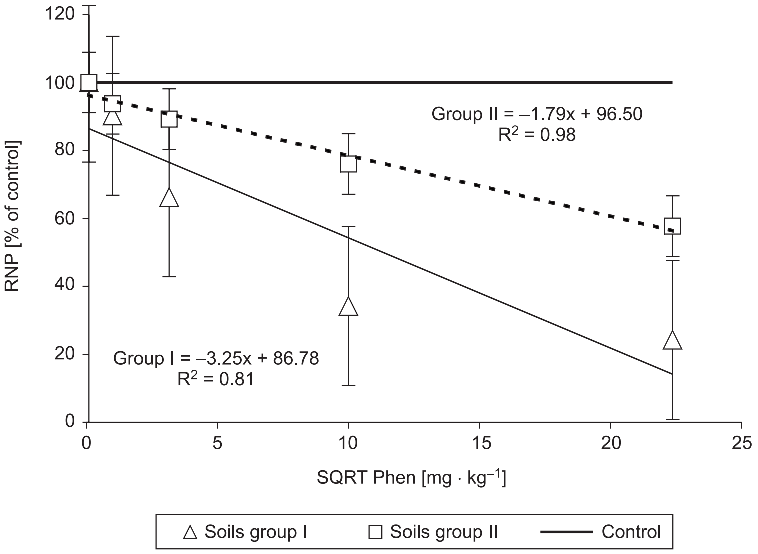
Table 3

Correlation coefficients (r) between soil properties and the effect (NP in % of control) of PAHs on nitrification potential

Soil property	All levels (n = 40)		Phen + Pyr (n = 16)			
	Phen	Pyr	1 mg · kg^{-1}	10 mg · kg^{-1}	100 mg · kg^{-1}	500 mg · kg^{-1}
fr. < 0.002 mm	0.29	0.38*	0.34	0.44	0.60*	0.47*
fr. < 0.02 mm	0.18	0.29*	0.27	0.23	0.42	0.36
C_{org}	0.23	0.41*	0.32	0.42	0.53*	0.48*
pH_{KCl}	0.27	0.63*	0.56*	0.66*	0.72*	0.64*
C:N	0.37*	0.65*	0.64*	0.75*	0.79*	0.72*
NP_{init}	0.34*	0.49*	0.41	0.59*	0.68*	0.62*
Σ13PAH	0.10	0.31*	0.36	0.33	0.21	0.32

Explanations as in Table 1; * statistically significant at the level of p ≤ 0.05.

To calculate the EC_x parameters, the effect-concentration relationships were evaluated following OECD guidelines [27]. Different linear regression models were tested for EC_{20} and EC_{50} calculations and on the basis of the r^2 values the square root-X regression was chosen as the best-fitting model giving the average r^2 of 85 % for Phen and 76 % for Pyr. The EC_{20} and EC_{50} data (with their 95 % confidence intervals) are given in Table 4; the EC_{50} parameters varied from 47 to 374 mg · kg^{-1} and from 28 to 279 mg · kg^{-1} for soils contaminated with Phen and Pyr, respectively (Table 4). For half of the soils, the effect of hydrocarbons was low, the predicted EC_{50} parameters exceeded the application limit of 500 mg · kg^{-1}. The EC_{20} parameters were within the limits of 14–296 mg · kg^{-1} for phenanthrene and 8–379 mg · kg^{-1} for pyrene.



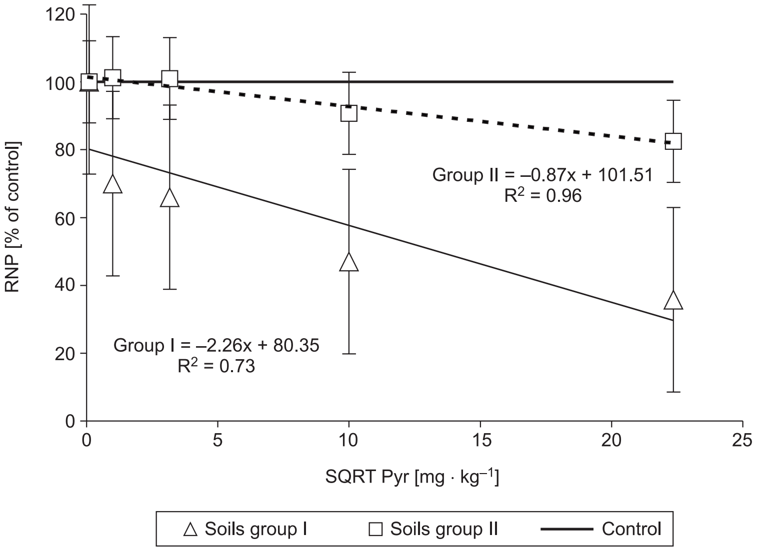


Fig. 2. Mean effects of Phen and Pyr on nitrification potential in two group of soils; group I – soils No 3, No 4, No 5, No 11; group II – soils No 6, No 7, No 8, No 12

In 60 % of evaluated combinations (8 soils × 2 PAHs) the LOEC values corresponded to the lowest applied concentration of 1 mg · kg^{-1}, while in the other cases it reached even 100 mg · kg^{-1}. Consequently, in majority of the samples the evaluated NOEC value was below 1 mg · kg^{-1} (Table 4).

Table 4

PAHs ecotoxicity parameters [mg · kg^{-1}] for soils under study

Parameter	No 3	No 4	No 5	No 6	No 7	No 8	No 11	No 12
Phenanthrene [mg · kg^{-1}]								
EC_{20}[a]	< 1	119 (78–182)	14 (3–38)	48 (21–103)	69 (57–83)	296 (181–498)	< 1	76 (54–105)
EC_{50}[a]	55 (19–144)	HAL	149 (86–260)	HAL	374 (330–425)	HAL	47 (9–192)	HAL
LOEC[b]	1	100	10	1	100	1	10	1
NOEC[b]	< 1	10	1	< 1	10	< 1	1	< 1
Pyrene [mg · kg^{-1}]								
EC_{20}[a]	< 1	8 (0–37)	287 (117–772)	379 (185–840)	NE	152 (121–192)	< 1	HAL
EC_{50}[a]	56 (26–115)	279 (152–534)	HAL	HAL	NE	HAL	28 (2–154)	HAL
LOEC[b]	1	1	1	1	NE	10	1	100
NOEC[b]	< 1	< 1	< 1	< 1	NE	1	< 1	10

[a] 20 and 50 % effect concentration evaluated on the basis of the best-fit square-root-x regression, in brackets – 95 % confidence interval; [b] evaluated on the basis of the results of ANOVA (one-way, Tukey HSD test, at $p \le 0.05$ level); NE – could not be estimated; HAL – extrapolated values above highest applied level.

Discussion

Presented results indicate that nitrification potential is a very sensitive parameter for description of the ecotoxicity of PAHs in freshly contaminated soils; the lowest observed effect corresponded to 1 mg · kg^{-1}. This is in agreement with opinion, that nitrifying bacteria are the most sensitive group of soil microorganisms exhibiting quick reaction to soil pollution [4, 6]. The negative impact of PAHs on soil nitrification processes was reported in other works, although the data varied widely. Some authors [28, 29] reported that application of phenanthrene at the level of 10 or 100 mg · kg^{-1} had no significant effect on nitrification. Ping and Tieheng [30] noted 6 % inhibition of nitrification in light soil contaminated with phenanthrene at the level of 250 mg · kg^{-1}. Sverdrup et al [12] observed 10 % decrease of soil nitrifying bacteria activity at the phenanthrene dose of 42 mg · kg^{-1}. Authors [12] noticed almost 60 % inhibition of nitrification after addition of Phen at the concentration ≥ 300 mg · kg^{-1}. In the same experimental conditions (one soil, C_{org} = 16.0 g · kg^{-1}, pH_{H_2O} = 6.2) pyrene exhibited lower toxic activity, the 10–20 % inhibition of NP occurred at the highest level of 3000 mg · kg^{-1} [12]. In the case of B[a]P the first significant effects for soil-nitrifying bacteria were recorded at 977 mg · kg^{-1} [2]. Remde and Hund [31] showed total inhibition of nitrification activity in soil contaminated with anthracene oil at concentration of 500 mg · kg^{-1}, at the same time the significant increase of the actual respiration rate was observed. Smreczak et al [15] noted that contamination of three soils (pH_{KCl} from 4.2 to 6.3; soil organic matter about 30 g · kg^{-1}) with Phen resulted in the 30–60 % inhibition of nitrifying bacteria activity at hydrocarbon levels ≥ 100 $\mathrm{mg \cdot kg^{-1}}$. The similar effect of Phen was found in the studies of Klimkowicz-Pawlas and Maliszewska-Kordybach [32]. Higher sensitivity of NP parameter to phenanthrene contamination was reported by Maliszewska-Kordybach et al [1] in the studies involving 50 soils of different properties; in 60 % of the samples statistically significant decrease of RNP value corresponded to Phen concentration of 10 $\mathrm{mg \cdot kg^{-1}}$. Inhibition of NP was observed by Klimkowicz-Pawlas and Maliszewska-Kordybach [32] and Maliszewska-Kordybach et al [1] in soils characterised by low organic matter content (OM < 12 $\mathrm{g \cdot kg^{-1}}$).

The observed stimulation of microbial activity at low doses of PAHs (Table 2) is known in the literature as "hormesis" and describes over-reaction of organisms in response to small deviations from the physiological norm [22]. At the low levels (≤ 10 $\mathrm{mg \cdot kg^{-1}}$) of soil contamination with phenanthrene or pyrene the increase in the dehydrogenases activity [14], nitrification potential [1] and intensity of respiration [3] was noticed.

Relatively higher ecotoxic effect of phenanthrene, as compared to pyrene, can be explained by the properties of the hydrocarbons. Water solubility of phenanthrene (1300 $\mathrm{\mu g \cdot dm^{-3}}$) is about 10 times higher than solubility of pyrene [11]. This property may decide about higher bioavailability and thus toxicity of this compound to soil organisms. The toxicity of hydrocarbons can be predicted using the QSAR (*Quantitative Structure Activity Relationships*) model, describing the relationship between the biological activity and physical-chemical properties (eg solubility) of compounds [12, 19]. In soils freshly contaminated with Phen (condition of the experiment) the bioavailable fraction of Phen (24 h extraction with Tenax) is relatively high and may reach 90 % [15]. Pyrene exhibits higher sorption affinity to soils organic mater, as expressed by its octanol/water partition coefficient [19]. Stronger binding to soil organic and mineral fractions diminishes PAHs bioavailability and toxicity [2, 3, 10].

Soils properties exhibited moderate, although significant, influence on ecotoxic effects of tested PAH compounds. The most important parameter was soil acidity regulating conditions for nitrifying bacteria development and processes [6, 33]; soils of lower pH exhibited also lowest NP values (Table 1). The effect of phenanthrene and pyrene was significantly lower in the group of soils of lower acidity and higher organic matter content (Fig. 2), which confirms that sorption processes of PAHs by mineral and organic soil fractions reduce their bioavailability – and thus their toxicity – to microorganisms [3, 7, 10]. This is supported by stronger influence of soil properties on the ecotoxicity of pyrene as compared to phenanthrene – Table 3.

Besides influence on soil sorption abilities, the high acidity of soils can create additional stress to nitrifying bacteria and thus increase their susceptibility to the effect of contaminants [3, 34]. The problems of the relationships between soils properties and ecotoxic effects of PAHs towards soil nitrifying bacteria were discussed wider in the earlier studies [1, 3, 5].

The suitability and application of NOEC and LOEC values in ecotoxicity studies is questionable [1, 27, 35] due to their dependency on the conditions of the experiment, on the concentration pattern used and on the statistical procedure applied. Our study indicates on much lower LOEC values (1 $\mathrm{mg \cdot kg^{-1}}$ for over 50 % of the data) as compared to the EC_{20} parameters; these are considered to be realistic "lowest effect" values assuming 20 % standard deviations in most of the ecotoxicity studies [27].

The high applicability of the square root regression for the calculation of the EC_{20} and EC_{50} parameters in the case of phenanthrene ecotoxicity was already proved in the earlier studies [1]. In this study the square root regression was the best fit equation in 45–60 % of calculations – Table 4. The received values varied widely from as low as 8 $mg \cdot kg^{-1}$ of EC_{20} for pyrene in soils No 4 (acidic, C_{org} content < 10 $g \cdot kg^{-1}$) to EC_{50} of 374 $mg \cdot kg^{-1}$ for phenanthrene in soil No 7 (neutral, C_{org} – 15.4 $g \cdot kg^{-1}$) – Table 4. There are limited data in the literature on ecotoxic parameters of PAHs, especially in relation to microorganisms. The EC_{50} calculated by Sverdrup et al [12] corresponded to 250 $mg \cdot kg^{-1}$ for Phen (nitrification end-point, maximum applied concentration – 3000 $mg \cdot kg^{-1}$), while EC_{10} for pyrene was 130 $mg \cdot kg^{-1}$. Higher ecotoxicity parameters were reported by Maliszewska-Kordybach et al [1]; the EC_{50} for the effect of Phen on nitrification potential were within the range of 165–1670 $mg \cdot kg^{-1}$ (50 different soils, 7 days incubation, maximum applied concentration – 1000 $mg \cdot kg^{-1}$). Relatively low PAHs toxicity towards soils microorganisms (evaluated on the basis of dehydrogenases activity) were observed in the studies of Klimkowicz-Pawlas and Maliszewska-Kordybach [13]; the EC_{50} values of 560–600 $mg\ \Sigma 2PAH \cdot kg^{-1}$ were reported for soils freshly contaminated with a mixture of anthracene and pyrene.

Conclusions

Contamination of soils with PAHs caused adverse effects on the activity of nitrification bacteria. The nitrification potential was a good indicator of the reaction of this sensitive group of microorganisms to the presence of PAHs. The effect was related to compound properties and soil characteristic. Stronger inhibition of nitrifying bacteria activity was observed in the case of phenanthrene, characterised by high water solubility and bioavailability. Effect of pyrene, exhibiting stronger sorption capability towards soil organic and mineral fractions, was more related to soil properties. Light soils with low organic matter content and low biological activity were more susceptible to PAHs toxic effects. High acidity created additional stress enhancing negative reaction of nitrifying bacteria on chemical contamination with PAHs.

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POTENCJAŁ NITRYFIKACJI JAKO WSKAŹNIK EKOTOKSYCZNOŚCI WWA W GLEBACH ŚWIEŻO ZANIECZYSZCZONYCH NA PRZYKŁADZIE FENANTRENU I PIRENU

Zakład Gleboznawstwa, Erozji i Ochrony Gruntów
Instytut Uprawy, Nawożenia i Gleboznawstwa – Państwowy Instytut Badawczy w Puławach

Abstrakt: Celem pracy była ocena możliwości zastosowania potencjału nitryfikacji jako wskaźnika ekotoksyczności WWA w stosunku do mikroorganizmów glebowych w glebach świeżo zanieczyszczonych. Oddziaływanie dwóch modelowych związków z grupy WWA (fenantrenu i pirenu) badano w warunkach laboratoryjnych (inkubacja gleb przez 7 dni w temperaturze 20 ± 2°C). Do badań zastosowano materiał glebowy pochodzący z warstwy ornej (0–20 cm) ośmiu gleb, z terenów użytkowanych rolniczo oddalonych od źródeł emisji WWA. Materiał glebowy sztucznie zanieczyszczano fenantrenem lub pirenem w ilości 1, 10, 100 i 500 $mg \cdot kg^{-1}$ gleby. Zanieczyszczenie gleb WWA spowodowało zahamowanie aktywności bakterii nitryfikacyjnych, które wydają się być czułym wskaźnikiem obecności WWA. Oddziaływanie węglowodorów było uzależnione od właściwości gleb oraz właściwości związków; najsilniejsze hamowanie potencjału nitryfikacji odnotowano w glebach lekkich o małej zawartości substancji organicznej oraz małej aktywności biologicznej zanieczyszczonych fenantrenem (charakteryzującym się dużą rozpuszczalnością w wodzie i biodostępnością). Dodatkowym czynnikiem stresowym dla bakterii nitryfikacyjnych była duża kwasowość gleb, która zwiększała ich wrażliwość na oddziaływanie zanieczyszczeń typu WWA.

Słowa kluczowe: potencjał nitryfikacji, wielopierścieniowe węglowodory aromatyczne, fenantren, piren, parametry ekotoksyczności

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

FACTORS CONDITIONING THE CONTENT OF MICROELEMENS IN THE MEADOW SWARD OF THE RADZIEJOWA REGION

UWARUNKOWANIA ZAWARTOŚCI MIKROSKŁADNIKÓW W RUNI ŁĄKOWEJ PASMA RADZIEJOWEJ

Abstract: Investigations were conducted in the Radziejowa Region (20.4079°–20.7147°E and 49.3988°–49.5421°N). 356 samples were collected on grasslands with different habitat conditions (height above sea-level, inclination, exposition) and differing in the way of their utilization. The sward varied in botanical composition and was classified into different phytosociological units. The subject of the analysis was to assess the content of macro- and microelements with the regard to environmental conditions.

In the area of the Radziejowa Region the mean contents of molybdenum and boron in the sward were low, for copper – quite low, for zinc – nearing the satisfactory content, for cobalt – satisfactory and for manganese – very high. Availability of microelements in the soil, except for manganese, was low. Regarding so low contents of analysed elements in the soil the correlation between the amount of the element extracted with 1 mol HCl $\cdot$ dm^{-3} and its content in the plant was not found, except for low correlation in the case of molybdenum. Out of many analyzed elements of particular communities there was correlation only between soil reaction and selected elements.

Keywords: meadow sward, trace elements, environmental factors

Chemical composition of meadow sward is very important in view of animal nutrition. Bulk feeds from permanent grasslands, particularly in mountain areas are the basic source of nutrients for ruminants. Husbandry and nutrition of this group of farm animals in the Carpathian Foothills is maintained in a traditional way. Potential intensification of cultivation measures was stopped due to low profitability. However, the sward use under such conditions most frequently leads to a negative nutrient balance. Systematic harvesting of hay yields at limited mineral fertilization and usually

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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 +48 12 662 4346, fax +48 12 662 4341, email: mkopec@ar.krakow.pl

[2] Department of Ecology, Climatology and Air Protection, University of Agriculture in Krakow, al. A. Mickiewicza 24, 31–120 Kraków, Poland.

at inferior fertilization with natural fertilizers (because of long distance from farms) worsens the already unfavourable situation of plant nutrition. Nutrient bioavailability may be affected also by the habitat conditions.

The investigations aimed at determining the factors conditioning the content of selected microelements in the sward of permanent grasslands from the mountain areas.

Material and methods

The research was conducted in the Radziejowa Region (20.4079°–20.7147°E and 49.3988°–49.5421°N), which is a part of the Beskid Sadecki Mts. Considering the geological structure the Beskid Sadecki is situated in the zone of Krynica Subunit, the Magura Nappe [1]. Mostly gleyed and leached brown soils formed in this area and less frequent acid brown soils (mainly podzolized and typical ones) [2]. According to Hess classification [3] the Radziejowa Region encompasses moderately warm, moderately cool and cool climatic belts.

Soil and plant samples were collected from grasslands with different habitat conditions (altitude above the sea level, land slope and slope aspect) and various types of management (Table 1).

Table 1

Statistics parameters of selected factors taken into account in testing environmental samples

Parameter	pH	Height	Inclination	Share [%]		Available form of soil $[\mathrm{mg \cdot kg^{-1}}]$	
		[m a.s.l.]	[°]	grasses	papilionaceous plants	P	K
Arithmetic mean	4.29	655.7	17.2	47.8	9.4	25.7	130.1
Standard deviation	0.57	147.2	8.22	14.8	9.0	23.3	72.4
Minimum	3.36	343	0	2.0	0.0	1.68	11.01
Maximum	6.53	963	40	87.1	47.1	167.8	510.1
Lower quartile	3.89	537	10	37.6	0.8	12.1	79.4
Upper quartile	4.57	778	20	57.5	13.3	31.4	161.4

In result the sward was characterized by a variable botanical composition and was classified to various phytosociological units. In 2006 the research conducted the previous year [4] was supplemented and the number of samples was increased about 145. Vegetation was described using Braun-Blanquet method in a total of 356 research points with the area of 100 m^2. In these areas a collective sample of vegetation was gathered and a collective soil sample from the root layer. The share of individual species groups (grasses, legumes and others) were computed on the basis of average percent of surface cover.

Maps of land use from the eighties of the 20th century were used for the investigations and on the basis of those permanent grasslands and permanent grasslands formed on arable lands were determined. Macroelement and microelement contents in the plant sample were determined by methods commonly used in agricultural chemistry, mainly ICP-AES technique after sample incineration and dissolving in nitric acid(V) (1:2). The soil pH was assessed by potentiometer in 1 mol KCl · dm^{-3}. Heavy metals were extracted from soil with 1 mol HCl · dm^{-3} solution [5] and regarded as potentially bioavailable forms.

Results and discussion

Determined ranges of desirable microelement content in view of forage suitability [6] allow for a conclusion that in the investigated area mean contents of molybdenum and boron in the sward were low, copper content close to a bottom limit of low content, zinc close to upper limit of satisfactory content, cobalt content was satisfactory whereas manganese content was very high (Table 2).

Table 2

Statistics parameters of element contents in the sward of grasslands from the investigated area

Parameters	Cu	Zn	Mn	Mo	B	Co
	[mg · kg^{-1}]					
Minimum	0.10	4.24	18.0	0.025	0.12	0.01
Maximum	10.4	184.6	952	3.22	20.6	0.40
Arithmetic mean	5.65	53.0	209.3	0.291	7.32	0.078
Standard deviation	1.32	25.5	138.9	0.301	2.84	0.052
Lower quartile	4.70	35.0	115	0.14	5.31	0.04
Upper quartile	6.40	63.2	274	0.36	8.73	0.10

Molybdenum and cobalt in sward revealed considerable variability (V = 103 and 66 %, respectively) in comparison with copper (V = 23 %) and boron (V = 38 %). The ranges of absolute values between the lower and upper quartile for copper and boron contents were equally small, which indirectly confirms the deficient values of these elements in the sward. Very high manganese content results from considerable acidification of the soils in this area. Fifty percent of the analyzed soils revealed reaction within the pH_{KCl} range from 3.89 to 4.57.

Boron abundance in the soil (Table 3) is assessed considering the soil pH. However, irrespective of pH value, mean contents of boron in the analyzed soils were significantly smaller than 0.8 mg B · kg^{-1}, which has been assumed as the limit value for low content at pH lower than 4.5. The value of upper quartile is lower than the arithmetic mean, which confirms very small contents of boron extracted with 1 mol HCl · dm^{-3}.

Assuming that these are acid soils and heavy or medium soils, typical for this area, their abundance in manganese may be estimated as medium. The range of mean abundance in soils with pH to 4.5 ranges from 16 to 180 mg Mn · kg^{-1} soil. This range comprises 50 % of the analyzed samples between the lower and upper quartile (Table 3).

Table 3

Statistics parameters of element contents extracted of 1 mole HCl · dm^{-3} in the soil from the investigated area

Parameters	Cu	Zn	Mn	Mo	B	Co
	[mg · kg^{-1}]					
Minimum	0.01	0.03	1.70	0.001	0.012	0.020
Maximum	1.15	4.79	129.9	0.300	1.140	1.106
Arithmetic mean	0.38	1.66	34.7	0.026	0.143	0.266
Standard deviation	0.14	0.63	14.9	0.025	0.184	0.099
Lower quartile	0.29	1.22	26.6	0.010	0.059	0.211
Upper quartile	0.44	1.98	42.1	0.030	0.134	0.313

The soil abundance in zinc extracted by 1 mol HCl · dm^{-3} was low, as has been demonstrated by the maximum zinc content in soil which was on the border of low and medium for soil with medium granulometric structure.

Very low contents of copper, as well as molybdenum (Table 3) were assessed in the soil, assuming its acid reaction and low abundance in bioavailable phosphorus.

Analysis of simple linear regression conducted for the relationship between the metal contents in plants and in 1 mol HCl · dm^{-3} extract demonstrated that the significant dependency was apparent only for molybdenum (r = 0.41) and zinc (r = 0.15).

Analysis of multiple regression was conducted for individual metal contents in the meadow sward and selected elements of the environment. The altitude were also considered above the different sea levels, land slopes, slope aspects and various types of land management, phytosociological groups, sward fractional composition and chosen elements of the soil chemical composition. The analysis did not reveal any effect of researched elements on the selected trace elements. On the other hand, significant dependencies were registered for the element content in sward:

– for Mn on pH (BETA = –0.38) and legume share (BETA = –0.26); $R^2 = 0.27$, F = 34.15;

– for Zn on exchangeable cations Ca (BETA = –0.25) and soil content of zinc extracted with $CaCl_2$ (BETA = 0.30); $R^2 = 0.21$, F = 24.8;

– for Co on pH (BETA = –0.31); $R^2 = 0.09$, F = 19.4;

– for Cu on the altitude above the sea level (BETA = –0.25); $R^2 = 0.06$, F = 12.8.

Generally the determined values point to a characteristic effect of soil reaction. The more acid the soil, the greater amounts of manganese, zinc and cobalt should be expected.

Copper content in soil revealed a decreasing tendency along with the altitude above the sea level.

The results presented above suggest that systematic use of mountain meadows of the Radziejowa Region leads to exhaustion of soil heavy metal reserves. In practice, fertilization with both mineral and natural fertilizers has decreased over that last years. Farmers do not attach importance to microelement fertilization on grasslands. Balance of trace elements under these conditions is generally negative [7–10]. On one hand elements are taken up with yields, on the other hand, they are either not supplemented or only a small amount is supplied in the ballast or natural fertilizers. In these conditions, the forage which perhaps several or many years ago met the requirements of the element content, currently reveals the contents below the recommended norms. The situation is getting worse and it is difficult to assess due to a lack of indicator plants. In the sward, species sensitive to possible deficiencies of trace elements will be replaced with others, which tolerate the low abundance. Trace element solubility in conditions of acid soils is also limited. Potentially bioavailable contents of elements in soil diminish. Sparingly soluble forms remain in soil, which not all plants can use during vegetation. Root secretions of some species may enable more intensive uptake to meet the plant requirements. The length of root system in individual plant species may be of crucial importance in these conditions. Formed soil horizons may be variously abundant in trace elements [11] and their potential deficiencies may condition plant regression visible as simplification of community structure and change of species composition. Because of a number of various interdependencies it is difficult to find habitat factors conditioning the variability of element content in the sward [12].

Conclusions

1. Research conducted in the area of the Radziejowa Region revealed that the sward from grasslands in a majority of samples revealed a low content of molybdenum and boron, sufficient content of zinc and cobalt and very high content of manganese, which denoted low abundance of soils from this region in the above-mentioned elements, except for manganese.
2. Statistical analysis of the data revealed a lack of significant correlation dependencies between the forms of potentially active microelements in soil and plants. Among a number of analyzed elements of individual communities only soil reaction revealed relationship with the selected elements.

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UWARUNKOWANIA ZAWARTOŚCI MIKROSKŁADNIKÓW W RUNI ŁĄKOWEJ PASMA RADZIEJOWEJ

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

Abstrakt: Badania prowadzono w paśmie Radziejowej (20,4079°–20,7147°E i 49,3988°–49,5421°N), gdzie pobrano 211 próbek na użytkach zielonych o zróżnicowanych warunkach siedliskowych (wysokość nad poziom morza, nachylenie, ekspozycja) oraz o różnym sposobie gospodarowania. Ruń charakteryzowała się zmiennym składem botanicznym i została zaklasyfikowana do różnych jednostek fitosocjologicznych. Przedmiotem analizy była ocena zawartości makroelementów i mikroelementów na tle warunków siedliskowych.

Na obszarze Pasma Radziejowej średnie zawartości w runi molibdenu i boru były niskie, miedzi – bliska dolnej granicy zawartości niskiej, cynku – bliska górnej granicy zawartości wystarczającej, kobaltu – wystarczająca i manganu – bardzo wysoka. Zasobność gleby w mikropierwiastki, z wyjątkiem manganu, była niska. W zakresie tak małych zawartości analizowanych pierwiastków w glebie nie stwierdzono zależności pomiędzy zawartością pierwiastka ekstrahowanego 1 mol HCl $\cdot$ dm^{-3} a ich zawartością w roślinie, z wyjątkiem słabej korelacji dla molibdenu. Spośród szeregu analizowanych elementów poszczególnych zbiorowisk tylko odczyn wykazywał zależność z wybranymi pierwiastkami.

Słowa kluczowe: ruń łąkowa, pierwiastki śladowe, czynniki środowiska

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Marcin LEMANOWICZ[1] and Andrzej GIERCZYCKI[1]

INFLUENCE OF ZETAG 63 SONICATION ON AGGREGATION AND BREAKAGE PROCESSES IN A TANK WITH TURBINE MIXER

WPŁYW SONIFIKACJI WYBRANEGO FLOKULANTU NA PROCESY AGREGACJI I ROZPADU KREDY W ZBIORNIKU Z MIESZADŁEM TURBINOWYM

Abstract: Flocculation process is commonly used in different industrial branches, eg in sewage sludge treatment. New methods are constantly developed for efficiency improvement or enhancement of other desirable end product features. It was proved that ultrasonic sonication of flocculant advantageously influences dewaterability parameters of sewage sludge. The final water content was decreased. Moreover, a half of dosage of the sonificated flocculant allowed one to achieve the electrokinetic potential equal to that achieved with a full dosage of the unmodified flocculant. An influence of ultrasonic sonication of the industrial flocculant ZETAG 63 on the particle size distribution of chalk suspension in distilled water is presented. Measurements were taken with the use of the laser particle size analyzer Frisch Analysette 22.

It was shown that sonication of flocculant had a negative impact on flocculation process and resulted with the decreased efficiency of polymer flocculating properties, ie the mean particle diameter decreased.

Keywords: aggregation, breakage, flocculation, ultrasounds, mixing

Aggregation process is commonly used in different industrial branches [1], eg in sewage sludge treatment. A typical goal is to enlarge a solid particle size in suspension for its easier removal. Then sludge is dewatered (eg via filtration), dried and utilized. As a flocculating agent different types of high-molecular weight cationic, anionic or nonionic polymers are used. When added to solid-liquid suspension they form branched flocks significantly larger than primary aggregates. This process runs in four steps [2]: mixing, adsorption of polymer on particle surface, reconformation and finally flocculation via branching phenomenon. As an alternative to the mentioned process the charge neutralization or charge electrostatic patch mechanisms may appear. This process is called in general the aggregation. However aggregates are simultaneously broken due to

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[1] Department of Chemical and Process Engineering, Faculty of Chemistry, Silesian University of Technology, ul. M. Strzody 9, 44–100 Gliwice, Poland, phone +48 32 237 1636, email: Marcin.Lemanowicz@polsl.pl

shear forces resulting from turbulent flow in a mixer. These two opposite phenomena compete during the process leading after a certain period of time to a steady state. It can be described mathematically by the general aggregation-breakage equation [3]:

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^v \beta_{ag}(v-u,u)\,n(u,t)\,n(v-u,t)\,du + \int_v^\infty b(v,u)\,\beta_{br}(u)\,n(u,t)\,du + \ldots$$
$$\ldots - \int_0^\infty \beta_{ag}(v,u)\,n(v,t)\,n(u,t)\,du - \beta_{br}(v)\,n(v,t) \tag{1}$$

where: first two expressions on the right-hand side of Eq. (1) represent the birth terms due to the aggregation and breakage and last two expressions represent the death terms due to the aggregation and breakage.

There are many attempts to enhance flocculation process [4] or to adjust different parameters of end product, eg dewaterability characteristic. Among the others, there are application of electromagnetic field [5], flocculant blends [6] or polymer-surfactant mixtures as flocculating agents [7]. A practical application of ultrasonic field was considered since the beginning of the 20th century [8]. At present, it is used in many ways, eg in surface cleaning [9], crystallization or extraction [10]. Ultrasounds have also found application in air [11] and water cleaning [12]. In power plants ultrasonic field is used to sonificate flue gases, which leads to aggregation of solid particles [13]. This is usually initial process before an electrofilter unit. Its goal is to remove larger particles from the gas stream and to aggregate smaller ones which would not be stopped in an electrofilter. In water treatment facilities ultrasounds may be used in many ways [14–17]. Among others there are sludge disintegration [18] or ultrasonic conditioning of excessive deposit [19]. Wolny [20] researched an influence of ultrasonic field on sludge structure and its dewaterability properties. She proved that ultrasonic sonication of flocculant had a positive influence on many properties of flocculated sludge, eg final water content or a value of electrokinetic potential.

Materials and measurement procedure

The experimental setup consisted of a mixing tank with the turbine, laser particle size analyzer Fritsch Analysette 22, peristaltic pump, ultrasonic horn and computer (Fig. 1).

In experiments the cylindrical mixing tank of a volume $V_{zb} = 5.39 \cdot 10^{-3}$ m^3 equipped with 4 baffles was used. The tank of inner diameter $D_{zb} = 0.19$ m was made of metaplex. The agitator (turbine) of diameter $8 \cdot 10^{-2}$ m was driven by the direct current engine Heidolph RZR 2102 control type (Heidolph Instruments GmbH). The turbine was placed $6 \cdot 10^{-2}$ m above the bottom of the tank. Suspension was drawn from the mixer by tubes and circulated in a closed system. After examination in the laser particle size analyzer the suspension came back to the tank. This experimental setup was based on the earlier research reports found in the literature [21, 22].

The ultrasonic horn VCX 130 by Sonics was used as a source of ultrasounds acting on flocculant. The horn was of 6 mm in diameter and length of 113 mm, made of

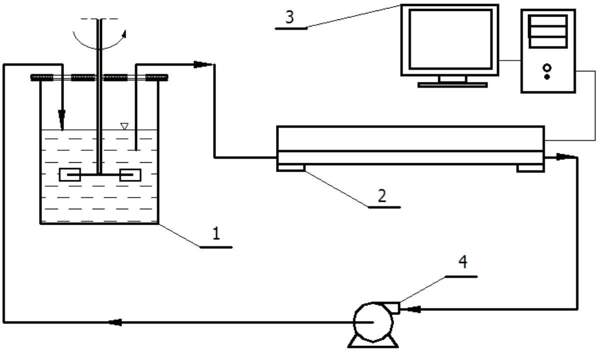

Fig. 1. Laboratory setup scheme: 1) mixing tank, 2) laser particle size analyzer, 3) computer, 4) peristaltic pump

titanium alloy TI-6AL-4V. It worked with the amplitude of 123 μm and frequency of 20 kHz. The power supply was equal to 130 W. The experimental medium used was the suspension of commercial chalk ($d_{32} \approx 2 \cdot 10^{-6}$ m) in distilled water. An amount of 1.5 g of chalk was weighted on the analytical balance and mixed with a small amount of distilled water. Such mixture was added to $5.39 \cdot 10^{-3}$ m^3 (full mixing tank) of distilled water. Chalk was added while the agitator was working. The amount of chalk was chosen in a way to assure optimal working conditions for the laser particle size analyzer.

Zetag 63 is a synthetic, high-molecular weight cationic polyacrylamide of medium charge, used mainly in sewage treatment processes. An appropriate amount of dry solid ZETAG 63 was poured to a flask of volume 50 cm^3, then 1.5 cm^3 of methanol was added to moisturize crystals and finally distilled water was added to achieve 0.1 % wt concentration of the solution. The flocculant was used 24 h after preparation. It was stored in a fridge at temperature about 5 ^oC, no longer than 4 days. Flocculant samples of a volume 10 cm^3 were sonificated in a glass beaker for different periods of time equal to 2, 4, 6, 8 and 10 seconds.

After addition of chalk (during mixing) to the mixing tank filled with distilled water a suitable measurement was taken (measurement zero). Then the flocculant was added (1.33 mg g^{-1} of chalk) using a pipette and the stopwatch started. Each flocculant was examined without and with sonification. Measurements were taken after 1, 3, 5, 10, 15 and 20 minute and repeated at least three times to eliminate measurement errors. A rotational frequency of the mixing turbine was set to 200 rpm.

Results and discussion

The dosage of 1.33 mg unmodified polymer per 1 g of chalk resulted in a significant enlargement of size of particles in suspension. A mean size of aggregates was about ten times greater in the end flocculation process (Fig. 2).

After the injection of polymer the particle size distribution (PSD) moved rapidly toward the high size classes. After the first minute the largest aggregates had a size

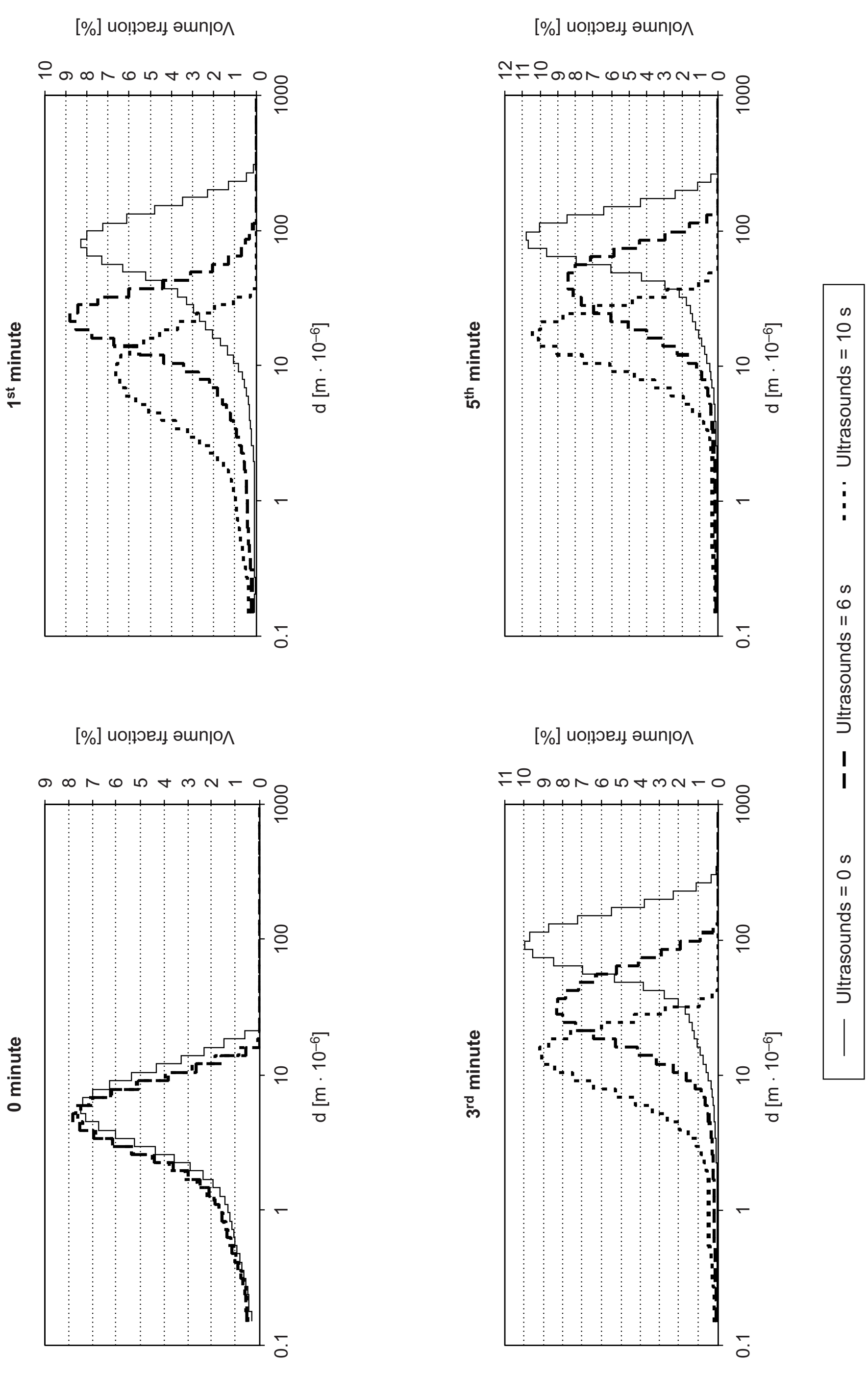

Fig. 2. The change of the particle size distribution during flocculation process for unmodified flocculant and sonicated for 6 and 10 seconds

above $3 \cdot 10^{-4}$ m. In steady state the PSD was unimodal with a size of all aggregates smaller than $2.5 \cdot 10^{-4}$ m. Although strong flocculating effect occurred, the lowest size class of $0.16 \cdot 10^{-6}$ m was still present in the suspension. During the process a decrease of turbidity was observed. In a case of the modified flocculants, the PSD is also unimodal in the steady state. But the mean size of particles is smaller than in a case of the unmodified flocculant which could be also seen via a change of turbidity. With the usage of flocculant sonificated for 10 seconds there are no larger aggregates than $50 \cdot 10^{-6}$ m in the suspension.

Ultrasonic sonication had a negative influence on flocculation process. In a case of ZETAG 63 the mean diameter of aggregates decreased with the time of sonication (Fig. 3). The largest changes were noticed during first six seconds of modification where d_{32}, ie volume to surface mean diameter, so called Sauter diameter, changed from $20 \cdot 10^{-6}$ m to $10 \cdot 10^{-6}$ m.

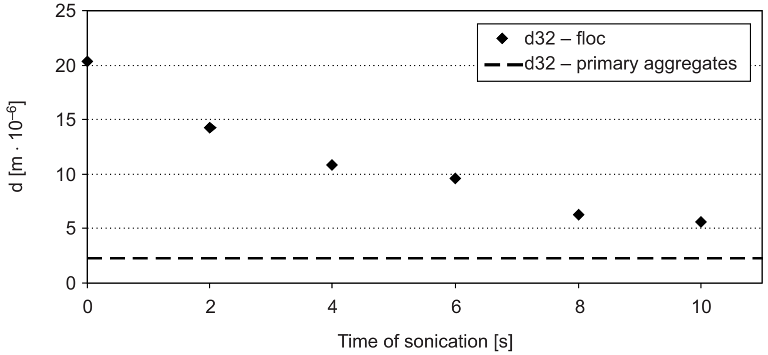

Fig. 3. Change of the Sauter mean diameter in the steady state vs time of sonication

Primary aggregates showed compact, oval structure (Fig. 4a). Flocks created with the unmodified flocculant were very branched and porous (Fig. 4b). They had a strongly developed 3D structure. During sonification the structure of polymer changed from long strongly branched chains to the short simple ones. This resulted with a change of flock structure – flocks became smaller and more compact (Fig. 4c).

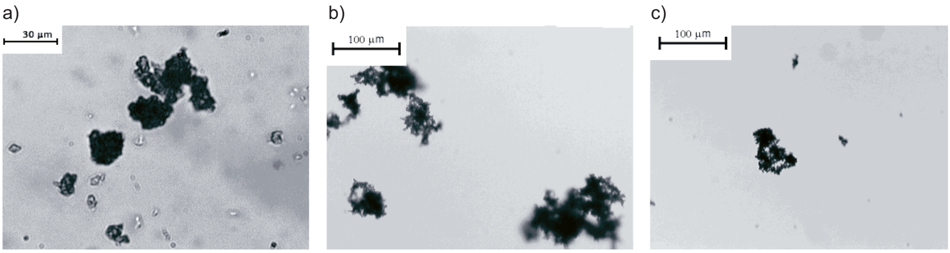

Fig. 4. Aggregates: a) before flocculation (primary aggregates), b) after flocculation with the unmodified flocculant, c) after flocculation with the flocculant sonicated for 6 seconds

Conclusions

In tested ranges of parameters ultrasonic sonication of ZETAG 63 flocculant had a negative influence on flocculation process. A mean diameter of flocks decreased with sonification time. The largest changes were observed within two to six seconds of modification. The polymer sonificated for ten seconds showed almost no flocculating properties. There were no significant changes in a PSD shape.

The polymer underwent ultrasonic degradation resulting in mid-chain scission. Modification of flocculant resulted in modified structures of the created flocks. They were less porous and had the poorly developed 3D structure.

Although ultrasonic sonication made worse flocculation properties of the polymer, a change of structure of flock is crucial for dewaterability properties of sludge. Typically less porous aggregates contain less water. Also their surface is "smoother" which results in a better packing in sludge. Summing up, one can conclude that wider research is needed to define a more general influence of ultrasonic sonification on different types of flocculants.

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WPŁYW SONIFIKACJI WYBRANEGO FLOKULANTU NA PROCESY AGREGACJI I ROZPADU KREDY W ZBIORNIKU Z MIESZADŁEM TURBINOWYM

Katedra Inżynierii Chemicznej i Procesowej, Wydział Chemiczny
Politechnika Śląska

Abstrakt: Proces flokulacji jest powszechnie stosowany w różnych gałęziach przemysłu, m.in. w oczyszczalniach ścieków. Wciąż poszukuje się nowych metod zwiększenia jego efektywności czy też poprawy innych, pożądanych cech produktu końcowego. Udowodniono, że ultradźwiękowa sonifikacja flokulantów korzystnie wpływa na parametry odwadniania osadów ściekowych. Zmniejsza ona końcową zawartość wody. Ponadto, połowa dawki nadźwiękawianego flokulantu pozwala osiągnąć potencjał elektrokinetyczny równy potencjałowi w przypadku użycia pełnej dawki niemodyfikowanego flokulantu. W pracy przedstawiono wpływ ultradźwiękowej sonifikacji przemysłowego flokulantu ZETAG 63 na rozkład ziarnowy zawiesiny kredy w wodzie destylowanej. Badania przeprowadzono przy wykorzystaniu laserowego analizatora ziarnowego Analysette 22 firmy Fritsch.

Wykazano, że sonifikacja flokulantu ma niekorzystny wpływ na proces flokulacji i skutkuje osłabieniem możliwości flokujących polimeru, tj. średni rozmiar ziarna zmniejsza się.

Słowa kluczowe: agregacja, rozpad, flokulacja, ultradźwięki, mieszanie

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Ryszard MAZUREK[1], Karolina SZYMAJDA[2]
and Jerzy WIECZOREK[3]

MERCURY CONTENT IN SOILS OF THE PIENINY NATIONAL PARK

ZAWARTOŚĆ RTĘCI W GLEBACH PIENIŃSKIEGO PARKU NARODOWEGO

Abstract: The work aimed at determining total mercury content in soils of the Pieniny National Park and relationship between properties of studied soils and mercury content. Soil samples used in the studies were collected from all genetic horizons of 12 profiles. Mercury concentrations in most part of investigated profiles (11 of 12) did not exceed limit content permissible for unpolluted soils. Mercury pollution was deposited mainly in organic and humus horizons. The highest content of mercury was determined in organic and humus horizons of some mountain humic rendzina on the top of the Biala Skala. Some of physical-chemical properties influenced profile distribution of mercury. Based on statistical analysis correlations were found between mercury accumulation and soil reaction (pH measured in 1 mol KCl $\cdot$ dm^{-3}), content of organic carbon and total nitrogen as well as clay fraction content (< 0.002 mm) in granulometric composition.

Keywords: mercury, soil, pollution, the Pieniny National Park

Mercury presence in soils is conditioned by natural factors (the content in the parent rock or volcanic eruptions) and by anthropogenic ones (gases and dusts from fuel combustion and technological processes) [1, 2]. Heavy metal accumulation in the area of the Pieniny National Park is mainly influenced by mountainous surface features, relatively heavy rainfall and location close to industrialized regions of Krakow and Silesia. Heavy metals, including mercury penetrate to the park area mainly as gases or dusts [3]. The most serious dust emitters in the park territory are home furnaces and petrol fumes, inevitably connected with intensified tourist traffic in this area [4].

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[1] Department of Soil Science and Soil Protection, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, email: rrmazure@cyf-kr.edu.pl

[2] Administrative Department, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, email: karolaszymajda@interia.pl

[3] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone +48 12 662 4349, fax +48 12 662 4341, email: rrwieczo@cyf-kr.edu.pl

The paper aimed at an assessment of the total mercury content in soils of the Pieniny National Park and determining relationships between selected properties of the analyzed soils and degree of this element accumulation in soil.

Material and methods

The investigations were conducted on soil material collected from genetic horizons of 12 soil profiles located on the territory of the Pieniny National Park (Fig. 1). Individual soil pits represent the following taxonomic units: brown rendzinas (1 profile), mountain humic rendzina (1 profile), brown pararendzinas (4 profiles), typical brown soils (1 profile), gleyed brown soils (2 profiles), leached brown soils (2 profiles) and ground gley soils (1 profile).

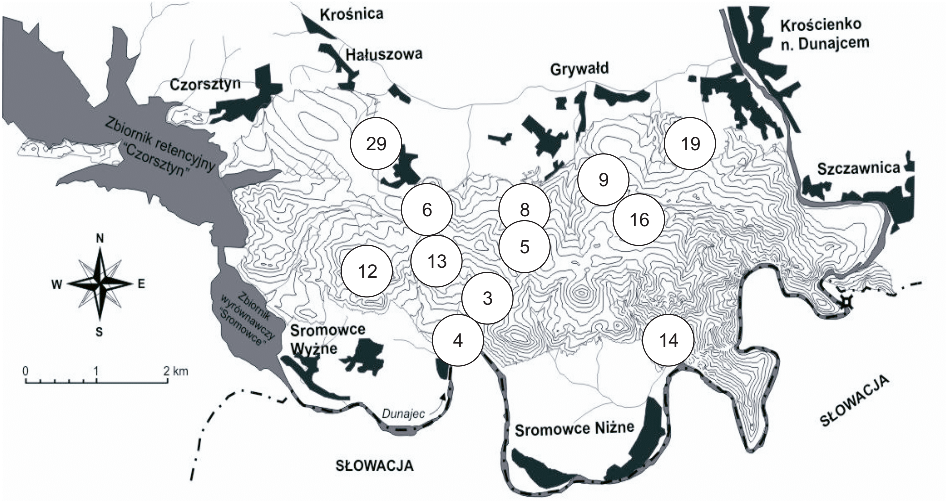

Fig. 1. Location of soil profiles

The soil material taken from individual genetic horizons was dried and sifted through a sieve with 2 mm mesh. The following assessments were made in the prepared soil samples:

– pH in distilled water and 1 mol · dm^{-3} KCl solution with potentiometric method,
– total nitrogen using Kjeldahl method in Kjeltec apparatus (Tecator),
– organic carbon according to Tiurin method modified by Oleksynowa,
– soil texture composition using Casagrande method in Proszynski's modification
– mercury content using atomic absorption spectrometry AAS in AMA 254 mercury analyzer (Altech).

The obtained results were verified statistically using Statistica 6.1 software; simple correlation coefficients were calculated and their significance was determined by t-Student test. Mercury accumulation indices (AI) were computed as a ratio of the element contents in the surface horizon and parent rock horizon of the profiles.

Results and discussion

A common characteristic of the analyzed soil from the Pieniny National Park was considerable content of skeleton in genetic horizons. Rendzinas (profiles 4 and 12) revealed granulation of light and heavy loams passing into clayey deposits in deeper profile horizons (Table 1).

Table 1

Physicochemical properties of investigated soils

Soil type, profiles number	Horizon	Content of fraction [%] with diameter [mm]				pH		Organic C	Total N
		1–0.1	0.1–0.02	< 0.02	< 0.002	H_2O	KCl	[$g \cdot kg^{-1}$]	
Rendzinas (2)	O A	— 18–38	— 12–34	— 26–36	— 2–34	5.4–6.7 7.5–7.7	6.9–7.1 5.1–6.4	203.2–251.2 31.4–59.2	16.0–18.9 3.6–7.0
Brown pararendzinas (4)	A	7–37	18–44	23–51	5–18	3.8–7.9	3.0–7.0	6.0–58.5	1.0–5.2
Typical brown soils (5)	O A	— 10–34	— 29–46	— 27–42	— 0–21	4.7 3.9–7.0	3.6 3.1–5.7	105.7 6.2–7.52	7.7 1.9–6.1
Ground gley soil (1)	A	46–50	23–32	16–22	1–0	5.0–6.4	4.7–6.1	65.9–74.2	3.8–5.6

In brown pararendzinas (profiles 6, 9, 14 and 19) determined granulation changed from light loams to clayey deposits. Brown soils (profiles 3, 5, 13, 16 and 29) were characterized by a granulation from light and medium loams in the surface horizons to heavy loams in their bottom horizons. A considerable part of sandy parts was visible among the fine parts of the analyzed ground gley soil (profile 8).

Table 2

Mercury content in genetic horizons of investigated soils

Profile nr	Soil type and subtype	Depth [cm]	Horizon symbol	Hg [$mg \cdot kg^{-1}$]
4	Brown rendzina	0–22	AhBbr	0.22
		22–40	BbrCca	0.09
12	Mountain humus rendzina	0–3	Ofh	0.32
		3–8	Oh	0.98
		8–55	AhCca	0.92
6	Brown pararendzina	0–10	Ah	0.24
		28–50	BbrCca	0.11
		50–110	Cca	0.10
9	Brown pararendzina	1–7	A	0.29
		7–29	BbrC	0.14
		29–42	IICca	0.34
		0–5	Ah	0.09

Table 2 contd.

Profile nr	Soil type and subtype	Depth [cm]	Horizon symbol	Hg [mg · kg^{-1}]
14	Brown pararendzina	5–16	ABbr1	0.08
		16–44	ABbr2	0.08
		44–73	ABbr3	0.10
		73–84	ABbrCca	0.09
		2–20	Ah	0.11
19	Brown pararendzina	20–44	ABbr	0.10
		44–62	BbrC1	0.13
		62–80	BbrC2	0.24
		0–12	Ah	0.09
3	Gleyed typical brown soil	12–45	Bbrg	0.10
		45–67	BbrCgg	0.08
		1–9	Ah	0.26
5	Leached typical brown soil	9–21	AhBbr	0.16
		21–52	Bbr	0.13
		52–90	BbrCca	0.10
		0–4	Ah	0.12
13	Typical brown soil	4–26	ABbr1	0.11
		26–39	ABbr2	0.12
		39–72	ABbrCca	0.13
		72–85	IICca	0.08
		0–2	O	0.18
16	Leached typical brown soil	2–12	Ah	0.12
		12–28	ABbr	0.09
		28–50	ABbrC	0.10
		> 50	C	0.14
		0–18	Ah	0.24
29	Gleyed typical brown soil	18–36	ABbr	0.14
		82–100	Cg	0.10
		0–30	Ahgg	0.15
8	Ground gley soil (humic)	30–44	AG	0.09

Rendzinas revealed reaction from acid to neutral in the organic horizons (pH_{H_2O} 5.4–6.7) and alkaline in the humus horizons (pH_{H_2O} ranged from 7.5 to 7.7). In the humus horizons of the analyzed pararendzinas the reaction fluctuated from very acid to alkaline (pH_{H_2O} 3.8–7.9). Brown soils revealed acid reaction in their organic horizons whereas in humus horizons the reaction varied from very acid to neutral. Ground gley soil was characterized by acid to slightly acid reaction in the humus horizons.

The highest content of organic carbon was assessed in organic horizons of the rendzinas (from 203.2 to 251.2 g · kg^{-1}). The highest content of organic carbon in humus horizons ranging from 65.9 to 74.2 g · kg^{-1} was characteristic for ground gley soil, lower contents were assessed in brown soils and pararendzinas, 6.2–75.2 g · kg^{-1} and 6.0–58.5 g · kg^{-1}, respectively (Table 1).

The analyzed soils of the Pieniny National Park (except profile 1) were characterized by mercury content lower than 0.5 g · kg^{-1}, which is a permissible value for protected area soils (Table 2) [5]. The highest mercury content (from 0.32 to 0.98 mg · kg^{-1}) was measured in rendzinas organic horizons. The content of mercury in the medium and bottom part of the mountain humic rendzina (profile 12) was the highest and exceeded the value of 0.90 mg · kg^{-1}. This profile was located on Biala Skala (805 m a.s.l.) in the western part of the Pieniny National Park and was particularly exposed to accumulation of pollutants carried from the Silesia Region. Mercury accumulation in genetic horizons of the analyzed rendzina was undoubtedly connected with this element absorption by raw organic horizons, which especially easily bind heavy metals [6].

In pararendzinas humus horizons A revealed Hg content between 0.09 and 0.29 mg · kg^{-1}, whereas elevated mercury content between 0.09 and 0.34 mg · kg^{-1} was assessed in parent rock Cca horizons. Small thickness of solum and considerable skeletal content affected free translocation of mercury into the soil profile and its accumulation in bottom horizons [7].

Mercury content assessed in organic and humus horizons of the investigated soils is approximate to this element content in other forest soils of southern Poland [8].

Characteristic elevated content of mercury in organic and humus horizons is connected with this element accumulation by organic matter at a low stage of decomposition. These horizons are a filter absorbing anthropogenic pollution (dusts), including mercury in the form of oxides and ions [1, 6, 9].

Computed values of accumulation index (AI) are low, which evidences a low mercury accumulation in the analyzed soils. Accumulation index values higher than 2 assessed for profiles: 4, 5, 6 and 29 prove a considerable accumulation of mercury in surface horizons as compared with the bottom ones (Fig. 2).

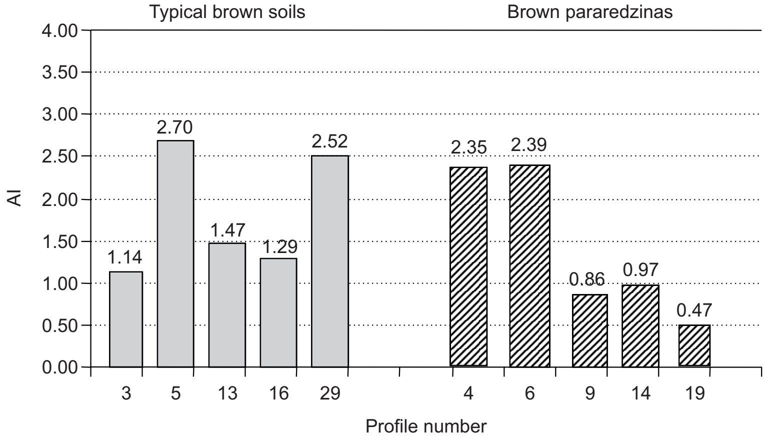

Fig. 2. Comparison of accumulation index (AI) calculated for brown soils proper and brown pararendzinas

In case of profile 3 among the analyzed brown pararendzinas it may be noticed that the value for accumulation index is lower than 1, which testifies an easy mercury translocation into the profile and accumulation mainly in bottom horizons of soil profiles.

Most soils in the Malopolska region is characterized by elevated mercury concentrations in comparison with the geochemical background, as shown by AI values higher than 1 [10]. Elevated accumulation indices (from 1.3 to 3.0) were also registered in the area of the Pieniny National Park for other heavy metals, ie Cd, Cu, Cr, Mn, Pb, Zn and Ni. It evidences slightly raised heavy metal accumulation in soils of this area [11].

Mercury content in organic horizons O and humus horizons A was connected with organic carbon and total nitrogen contents, and simple correlation coefficients calculated for these relationships were $r_{0.01} = 0.58$ and $r_{0.001} = 0.63$, respectively (Table 3). The other properties which positively affected mercury accumulation in the profile were: soil pH in KCl ($r_{0.05} = 0.43$) and the content of < 0.002 mm fraction ($r_{0.01} = 0.53$). The relationship between mercury content in soils, organic carbon content, share of floatable particles and additionally with sorption capacity and hydrolytic acidity was also confirmed by other authors [12, 13].

Table 3

Linear correlation coefficient between mercury content in organic (O) and humus (A) horizons and properties of investigated soils

Soil properties	Linear correlation coefficient (r)
pH H_2O	0.27
pH KCl	0.43*
Organic C content	0.58**
Total N content	0.63***
C:N ratio	0.26
Content of fraction < 0.02 mm	0.36
Content of fraction < 0.002 mm	0.53**

Significance level: * – $\alpha = 0.05$***; ** – $\alpha = 0.01$; – $\alpha = 0.001$.

Conclusions

1. A majority of soils in the Pieniny National Park revealed lower contents of mercury than the limit value assumed for the protected areas.
2. The greatest content of mercury was assessed in organic and humus horizons of the analyzed rendzinas.
3. Values of accumulation index (AI) show that a majority of the analyzed soils was characterized by an elevated content of mercury in comparison with geochemical background.
4. On the basis of statistical analysis it was demonstrated that mercury content in organic and humus horizons of the soils was positively correlated with the contents of organic carbon, total nitrogen, soil pH in KCl and the share of floatable particles (< 0.002 mm).

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ZAWARTOŚĆ RTĘCI W GLEBACH PIENIŃSKIEGO PARKU NARODOWEGO

Katedra Gleboznawstwa i Ochrony Gleb
Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem pracy było oznaczenie całkowitej zawartości rtęci w glebach Pienińskiego Parku Narodowego oraz określenie zależności między wybranymi właściwościami badanych gleb a stopniem akumulacji tego pierwiastka w glebie. Do badań pobrano próbki ze wszystkich poziomów genetycznych 12 profilów gleb. Większość profilów (11 spośród 12) charakteryzowała się mniejszą zawartością rtęci niż wartość przyjęta dla niezanieczyszczonych gleb obszarów chronionych. Największe zawartości rtęci zanotowano w poziomach organicznych i próchnicznych badanych gleb. Niektóre właściwości fizyczne i chemiczne gleb wpłynęły na przestrzenne rozmieszczenie rtęci w profilach glebowych. Biorąc pod uwagę współczynnik akumulacji (WA), większość badanych gleb charakteryzowała się podwyższoną zawartością rtęci w porównaniu z tłem geochemicznym. Na podstawie analizy statystycznej stwierdzono, że zawartość rtęci w poziomach organicznych i próchnicznych badanych gleb była skorelowana z wartością pH (mierzoną w 1 mol KCl $\cdot$ dm^{-3}), zawartością węgla organicznego i azotu ogólnego oraz z udziałem części spławianych (< 0.02 mm) w składzie granulometrycznym.

Słowa kluczowe: rtęć, gleby, zanieczyszczenie, Pieniński Park Narodowy

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Agnieszka MEDYŃSKA[1] and Cezary KABAŁA[1]

HEAVY METALS CONCENTRATION AND EXTRACTABILITY IN FOREST LITTERS IN THE AREA IMPACTED BY COPPER SMELTER NEAR LEGNICA

ZAWARTOŚĆ I ROZPUSZCZALNOŚĆ METALI CIĘŻKICH W PRÓCHNICACH LEŚNYCH NA TERENACH ZDEGRADOWANYCH PRZEZ HUTNICTWO MIEDZI

Abstract: Three permanent study areas, each consisting of four sampling sites, located at distances of 500, 1500 and 2100 m from emission source, were established in poplar plantings surrounding a large copper smelter near the town Legnica in Lower Silesia region of SW Poland. Total content as well as water and acetic acid extractable contents of Cu, Zn, Fe, Ca and Mg were analyzed in samples of forest litter (ectohumus) collected in November 2007. The total content of Cu reached 9590 mg · kg^{-1}, and Zn – 4020 mg · kg^{-1} d.m. in the site located 500 m away of smelter, and rapidly decreased with distance, while the content of Fe, Ca and Mg decreased insignificantly. Up to 0.5 % of total Cu and up to 1.2 % of total Zn was in water-extractable form, while 0.11 mol · dm^{-3} acetic acid released up to 7.2 % of Cu and 41 % of Zn, and more than 50 % of total Ca and Mg. Copper and zinc are immobilized in alkaline litter under poplar stands surrounding copper smelter, but any factor acidifying the litter may rapidly enhance solubility of accumulated heavy metals.

Keywords: heavy metals, solubility, extractability, copper industry, forest litter, soil pollution

The natural balance of the biogeochemical cycles has been considerably changed by the human activity causing enhanced mobilization of chemical elements in the environment as compared with the natural processes. Therefore, the essential processes of matter and energy cycling may become harmful [1]. Heavy metal accumulation in forest soil may effect nutrient cycling throughout the whole ecosystem by inhibiting litter decomposition and subsequently reducing the supply of nutrients released by mineralization [2]. Heavy metals can also have toxic effects on roots and mycorhiza fungi resulting in seriously reduction of nutrient uptake [3]. Forest humus, which has a large cation binding capacity, and provides relatively stable bindings with most of elements or theirs compounds plays a significant role in trace element accumulation

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[1] Institute of Soil Science and Environmental Protection, Wroclaw University of Life and Environmental Sciences, ul. Grunwaldzka 53, 50–357 Wrocław, Poland, phone +48 71 320 5604, email: jagamedynska@yahoo.com, cezary.kabala@up.wroc.pl

[4–6] and in returning nutrients to the soil through decomposition [7]. The principal fate during litter decomposition and mineralization is rather well established only for limited number of forest environments, mainly unpolluted [8–11], while the dynamics of chemical elements in forest litter and soils contaminated with excessive amounts of heavy metals is still scarcely known [12–15].

The aim of the present work was to evaluate the potential risk of soil contamination by the determination of the total accumulation of trace metals in forest floor humus near large copper smelter Legnica (south-western Poland), and the potential mobility of metals as studied by water extracts from forest litter.

Material and methods

The Legnica copper smelter is a part of the mining and metallurgy complex founded in 1951, which currently includes 4 mines, 3 ore enrichment plants and 3 smelters [16]. The complex has been producing approximately 500 000 tons of copper annually, one fourth of that is produced in the Legnica smelter. Copper smelting was connected in the past with a large emission of metal-containing dust, significantly reduced during the 1980s and 1990s in all the facilities comprised in the complex [17]. Long-term copper smelting in the Legnica area has however resulted in an extensive soil contamination with number of trace elements.

Three permanent study sites, each consisting of four sampling points (“replicates”), were established in the poplar plantings surrounding the copper smelter near the town Legnica in Lower Silesia region of SW Poland. Study sites are located at distances of 500 m (Site 1), 1500 m (Site 2) and 2100 m (Site 3) north-west from emission source, within so-called “sanitary zone” surrounding the smelter (Fig. 1).

All three afforested sites are situated on similar soils, Cutanic Luvisols [18] developed of loess-like sediments, having a texture of silt loam and nearly neutral reaction in surface mineral soil horizons.

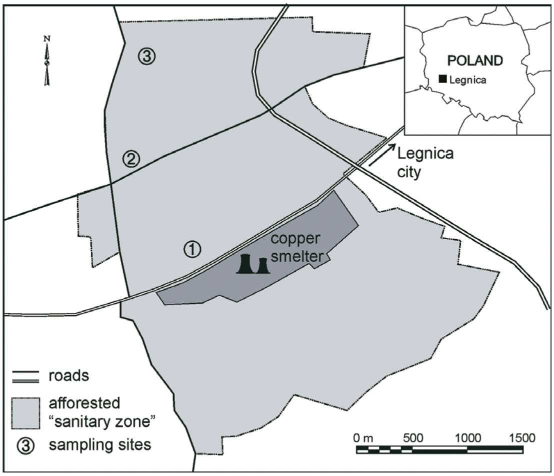


Fig. 1. Location of sampling sites near a copper smelter Legnica

The term "forest litter" used in this paper means all organic materials deposited at forest floor, including fresh litter (fresh leaves fall) and proper ectohumus, consisting of better decomposed plant residues. The overall thickness of sampled litters (including fresh fall) varied from 4–5 cm on Site 3 up to 8–10 cm on Site 1. Bulk samples of forest litter were collected in November 2007 in four replicates on each sampling site by using a steel cylinder (diameter 23 cm, sampling area 415 cm^2). All replicates were stored and analyzed separately.

General aim of study was to assess the total content of elements stored in forest litter and the potential of elements leaching by determination of their extractability under actual environmental conditions. Distilled water was selected as a substitute of rain water washing the litter, and the 0.11 $mol \cdot dm^{-3}$ acetic acid was used as one of proposed substitutes of natural acidic excretions of plant roots and fungal hyphens [17]. Fresh samples of litter were weight, crumbled and mixed by hand. Dry mass of samples in 105 ^oC was than determined to establish the comparable amounts of litter in extraction mixtures. Water-extractable and acetic acid-extractable forms of elements were determined using the fresh litter samples extracted with distilled water or 0.11 $mol \cdot dm^{-3}$ acetic acid in a suspension 1:10 m/v (litter : liquid). The total content of elements was determined after sample digestion with *aqua regia* ($HCl:HNO_3$ ratio 3:1) using microwave oven (in high-pressure PTFE beakers). Measurement of metal concentration in water and acid extracts was made using the flame atomic absorption spectroscopy (FAAS). All extractions were made in two laboratory replicates of each sample. Quality of determination has been monitored using soil reference materials (NIST-1515, IAEA-V-10) with certified total content of trace elements being analysed.

The variability of litter properties and content of elements on particular sites was evaluated by use of Duncan's multiple range test at $p < 0.05$.

Results and discussion

Although all forest litters were collected under the poplar stands of the same age, composition and canopy density, they significantly differed in thickness and mass of organic layer, as well as in the stage of decomposition. Forest litters collected on sites 2 and 3, located 1500 and 2100 m away from the smelter had at sampling time in November 2007 significantly smaller thickness and weight than the litters on site 1 located 500 m from the smelter (Table 1).

The difference in ectohumus thickness results not from higher biomass productivity in the stands near the smelter, but rather from reduced decomposition of leaves and their accumulation in thin compressed layers in successive years. Forest litters on sites 2 and 3 (1500 m and 2100 m away from the smelter) consisted mainly of freshly fallen leaves which confirms high rate of biomass decomposition in these areas.

All forest litters under examination have astonishingly high pH values, in a range of alkaline reaction in distilled water (Table 1) and very high total concentrations of calcium and magnesium, up to 2.9 % and 0.36 % of dry litter mass, respectively (Table 2).

Table 1

Characteristics of forest litter (ectohumus) on permanent study sites
near the copper smelter Legnica

Parameter	Distance from the smelter [m]		
	500	1500	2100
Fresh mass of litter [g · m^{-2}]	10.8^{*a} 8.2–13.5**	4.6^{b} 1.2–6.4	4.9^{b} 3.9–5.8
Dry mass of litter [g · m^{-2}]	4.0^{a} 3.0–4.9	1.6^{b} 0.4–2.5	1.6^{b} 1.3–1.9
pH_{H_2O} of litter (fresh mass)	6.9^{a} 6.6–7.2	7.0^{a} 6.8–7.1	6.9^{a} 6.3–7.3

Explanation: * – arithmetic mean, ** – range of results (minimum – maximum), $^{a, b, c}$ – homogeneous groups of Duncan's multiple range test (at $p < 0.05$).

Table 2

Total content of elements [mg · kg^{-1} d.m.] in forest litter (ectohumus)
on permanent study sites near the copper smelter Legnica

Element	Distance from the smelter [m]		
	500	1500	2100
Cu	9160^{*a} 8810–9590**	1282^{b} 1100–1450	472^{c} 303–610
Zn	2710^{a} 1680–4020	390^{b} 340–440	320^{b} 140–520
Fe	5565^{a} 3640–10160	2975^{b} 1600–3960	3460^{b} 2120–3540
Ca	22500^{a} 9600–29000	19300^{a} 12000–24400	21100^{a} 11000–27600
Mg	3045^{a} 2460–3340	3455^{a} 2780–3600	2055^{b} 1860–2440

Explanation: * – arithmetic mean, ** – range of results (minimum – maximum), $^{a, b, c}$ – homogeneous groups of Duncan's multiple range test (at $p < 0.05$).

Such properties of litters are evidences for pollution with alkaline dust emitted by smelter these days or in the recent past. Chemical composition of the dust emitted by the smelter was not determined, however, up to 11 % of total Ca and up to 12 % of total Mg amount in litter was found in water-extractable form (Table 3), which confirms that considerable part of these elements exists on plant residues as oxides easily soluble in water. Extraction with 0.11 mol · dm^{-3} acetic acid released 42–56 % of total Ca and 52–64 % of total Mg, indicating high potential solubility of calcium and magnesium compounds in litters in all three sites afforested with poplar trees around the copper smelter. Acetic acid-extractable forms may mobilize under any acidifying conditions, including acidic atmospheric precipitation, introduction of "acidifying" plant species, as birch, oak or coniferous trees, as well as an increasing activity of microorganisms in the rhizosphere.

Total contents of copper, zinc and iron (ie determined in *aqua regia*) in litter horizons in the surrounding of the copper smelter were much higher than found under natural deciduous forests in central Europe [5, 6] reflecting negative influence of smelter activity on an adjacent environment. The content of copper in Site 1 (500 m away from smelter) reached nearly 1 % d.m. mass – 9160 mg · kg^{-1} (in average), and in Site 2 and Site 3 decreased to 1282 mg · kg^{-1} and 472 mg · kg^{-1} d.m., respectively (Table 2). Mean contents of copper in particular monitoring sites situated at increasing distance from the smelter differ (decrease) significantly that was confirmed with Duncan's multiple range test. Similarly, the highest content of zinc (2710 mg · kg^{-1} d.m. on average) was found in the nearest surrounding of the smelter and significantly decreased with the distance, to 320–390 mg · kg^{-1} at 1500–2100 m from the smelter. Total amount of copper and zinc in the litter on Site 1 (500 m from the smelter) was even twenty times, and nine times higher, respectively, than on Site 3 located 2100 m from the source of emission. Total content of iron was also significantly higher in the forest litter on Site 1 (mean value 5565 mg · kg^{-1} d.m.) than on Sites 2 and 3 (2975 mg · kg^{-1} and 3460 mg · kg^{-1} d.m., respectively), but differences between studied areas were smaller than these found for copper and zinc.

Table 3

Concentration of water-extractable forms of elements [mg · kg^{-1} d.m.] in forest litter (ectohumus) on permanent study sites near the copper smelter Legnica

Element	Distance from the smelter [m]		
	500	1500	2100
Cu	12.0*^{a} 9.8–15.2**	6.2^{b} 4.2–8.6	2.3^{c} 0.6–5.1
Zn	7.1^{a} 5.0–8.5	4.6^{b} 1.7–10.9	2.2^{c} 0.73–3.8
Fe	3.0^{c} 0.9–4.3	9.0^{a} 2.5–13.8	6.4^{b} 4.2–7.7
Ca	2548^{a} 850–4015	2125^{a} 305–3257	1710^{b} 1210–2624
Mg	142^{a} 108–167	268^{b} 119–565	254^{b} 197–338

Explanation: * – arithmetic mean, ** – range of results (minimum – maximum), $^{a, b, c}$ – homogeneous groups of Duncan's multiple range test (at $p < 0.05$).

Extraction with use of distilled water released only 0.13–0.5 % of the total content of copper, however, due to the high total concentration of copper in litter, the amount of water-extractable copper in the litter was relatively high, in the range of 2.3 to 12.0 mg · kg^{-1} d.m. The amount of water-extractable zinc was similar to copper, in the range of 2.2 to 7.1 mg · kg^{-1} d.m., at relatively higher extractability in water (0.3–1.2 % of the total Zn amount). The amounts of the water-extractable copper and zinc decrease significantly with the increasing distance to the smelter (Table 3). The solubility of iron followed another rules, while the highest concentration of water-extractable iron was measured on Site 2 (1500 m to the smelter) – on average 9.0 mg · kg^{-1} d.m., and the lowest – ca 3.0 mg · kg^{-1} on Site 1 (500 m to the smelter). Relative extractability of iron in distilled water was the least among studied elements, ranging from 0.05 to 0.3 % of the total iron content.

Extraction with 0.11 mol · dm^{-3} acetic acid, imitating natural root secretions, revealed significantly higher solubility of trace elements as compared with the extraction with distilled water (Table 4).

Table 4

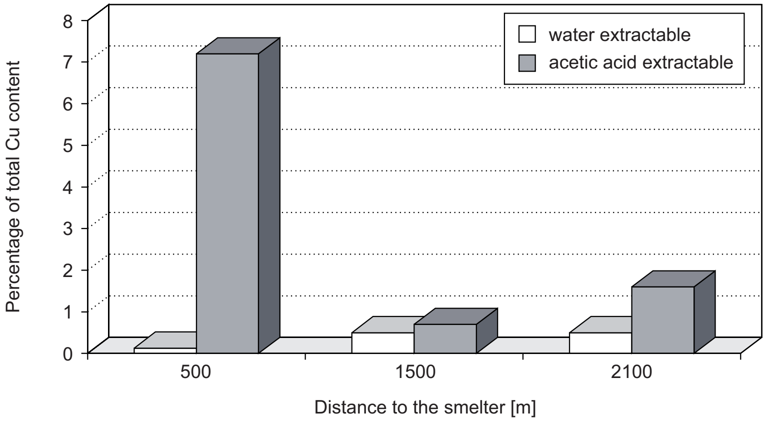
Concentration of 0.11 mol · dm^{-3} acetic acid-extractable forms of elements [mg · kg^{-1} d.m.] in forest litter (ectohumus) on permanent study sites near the copper smelter Legnica

Element	Distance from the smelter [m]		
	500	1500	2100
Cu	677*^{a} 171–1577**	8.7^{b} 6.6–9.8	7.9^{b} 1.8–10.9
Zn	1116^{a} 844–1460	117^{b} 101–140	101^{b} 31–131
Fe	10.7^{a} 8.1–16.1	13.0^{a} 8.9–14.6	10.8^{a} 2.4–26.5
Ca	12690^{a} 10650–15540	8370^{b} 7350–9210	8820^{b} 7500–10590
Mg	1747^{a} 1577–1927	1792^{a} 1584–2276	1319^{b} 1200–1423

Explanation: * – arithmetic mean, ** – range of results (minimum – maximum), $^{a, b, c}$ – homogeneous groups of Duncan's multiple range test (at $p < 0.05$).

Copper concentration measured in acetic acid extracts on Site 1 (500 m to the smelter) reached values up to 1577 mg · kg^{-1} d.m. (on average 677 mg · kg^{-1}), ie 7.2 % of the total content of copper in examined litters. Zinc concentration reached 1460 mg · kg^{-1} (on average 1116 mg · kg^{-1}), ie about 41 % of the total Zn content in the litter. Such a large extractability of copper and zinc in acetic acid means that these metals occur in the examined litters as compounds easily soluble in acids – eg oxides and carbonates, rather than in stable complexes with organic matter. The amount of acetic acid-extractable copper decreases rapidly with the distance to the smelter, from 677 mg · kg^{-1} d.m. (on average) on Site 1 (500 m to the smelter) to 8.7 mg · kg^{-1} (on average) on Site 2 (1500 m to the smelter). The ratio of metal content (both copper and zinc) extracted with 0.11 mol · dm^{-3} acetic acid to those extracted with distilled water becomes narrower with the distance to the smelter (Fig. 2). On all sites the ratio is significantly wider for zinc than for copper, probably due to higher susceptibility of zinc compounds to acidic solutions. The amounts of iron extracted with 0.11 mol · dm^{-3} acetic acid were similar on all studied sites, in the range from 10.7 to 13.0 mg · kg^{-1}, and were close to the amounts of water-extractable iron forms. Relative extractability of iron with acetic acid was on the level of 0.2–0.4 % of its total amount. Such a small solubility of iron confirms the strong binding of this element in insoluble compounds such as silicates, or in stable complexes with organic matter.

The results of the study show that organic horizons of the forest floor in an immediate surrounding of copper smelter near Legnica are strongly polluted with



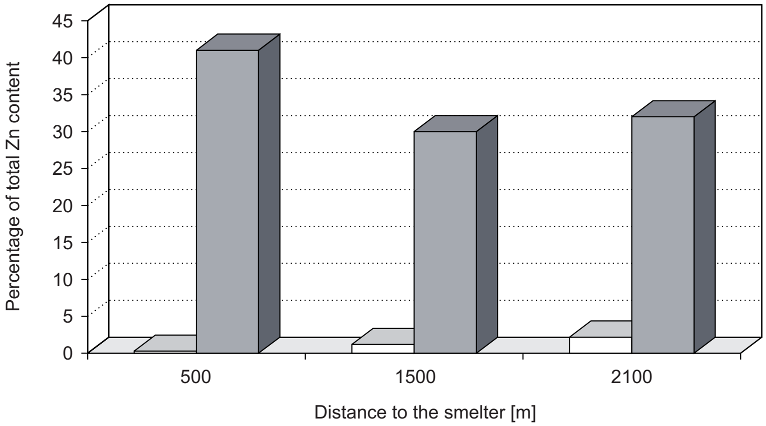


Fig. 2. Extractability of Cu and Zn (as a percentage of total content of the metals) in forest litter on permanent study sites near the copper smelter Legnica

copper and zinc, and, to a lesser extent, with iron. All these metals occur presently in relatively stable forms under alkaline reaction of the litter. Extraction with weak acids causes however large increase in solubility of examined metals, following the dissolution of calcium and magnesium compounds (oxides and/or carbonates). It means that organic horizons of forest floor may accumulate heavy metals from atmospheric pollution under specific conditions only. Any change in forest composition by an introduction of some deciduous or coniferous species, or the application of physiologically acidic fertilizers may lead to the acidification of forest litter and to the increase of solubility and mobility of previously accumulated heavy metals [2, 10, 11, 13]. Similar effect may cause natural rain precipitation correlated with reduction of alkaline dust emission from the smelter, as well as the raising of organic matter decomposition under decreasing litter contamination which follows the reduction of emission of metal-bearing industrial dusts [15].

Conclusions

1. Copper and zinc occur in highly contaminated and alkaline forest litters under poplar stands in the surrounding of copper smelter Legnica in relatively stable forms, weakly soluble in distilled water, that may extract only 0.13–0.50 % of total Cu and 0.3–1.2 % of total Zn content in forest litter.

2. Extraction with weak organic acid (as 0.11 mol $\cdot$ dm^{-3} acetic acid) releases up to 677 mg $\cdot$ kg^{-1} of copper (ie 7.2 % of the total Cu content in litter) and up to 1116 mg $\cdot$ kg^{-1} of zinc (ie 41 % of the total Zn content) from forest litter deposited in close surrounding of the smelter.

3. Any natural or anthropogenic changes in poplar stands, as mineral fertilization or introduction of coniferous tree species, that acidify the forest floor may significantly enhance solubility and mobility of metals accumulated presently in the ectohumus layer.

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ZAWARTOŚĆ I ROZPUSZCZALNOŚĆ METALI CIĘŻKICH W PRÓCHNICACH LEŚNYCH NA TERENACH ZDEGRADOWANYCH PRZEZ HUTNICTWO MIEDZI

Instytut Nauk o Glebie i Ochrony Środowiska
Uniwersytet Przyrodniczy we Wrocławiu

Abstrakt: Trzy stałe powierzchnie obserwacyjne, każda obejmująca po cztery punkty pobierania próbek, zlokalizowane w odległości 500, 1500 i 2100 m od źródła emisji zostały założone na obszarze zadrzewionym topolą wokół dużej huty miedzi w pobliżu Legnicy, w południowo-zachodniej Polsce. W próbkach próchnic nadkładowych pobranych w listopadzie 2007 r. analizowano całkowitą zawartość Cu, Zn, Fe, Ca i Mg oraz zawartość form rozpuszczalnych w wodzie i 0,11 mol · dm^{-3} kwasie octowym. Całkowita zawartość miedzi w ściółce osiągała poziom 9590 mg · kg^{-1} suchej masy, a cynku – 4020 mg · kg^{-1} s.m. na powierzchni zlokalizowanej 500 m od huty i raptownie zmniejszała się wraz z odległością. Zawartość Fe, Ca i Mg w ściółkach również zmniejszała się wraz z odległością, lecz w znacznie mniejszym stopniu niż Cu i Zn. Do 0,5 % całkowitej zawartości Cu i do 1,2 % całkowitej zawartości Zn występowało w analizowanych ściółkach w formach rozpuszczalnych w wodzie destylowanej. 0,11 mol · dm^{-3} kwas octowy uwalniał nawet do 7,2 % całkowitej zawartości Cu i do 41 % całkowitej zawartości Zn oraz ponad 50 % całkowitej ilości Ca i Mg. Miedź i cynk są słabo rozpuszczalne w warunkach alkalicznego odczynu próchnic nadkładowych w drzewostanach topolowych, lecz jakichkolwiek naturalny lub antropogenny czynnik prowadzący do zakwaszenia ściółek może spowodować raptowny wzrost rozpuszczalności nagromadzonych metali ciężkich.

Słowa kluczowe: metale ciężkie, rozpuszczalność, przemysł miedziowy, ściółki leśne, zanieczyszczenie gleb

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Marcin NIEMIEC[1] and Barbara WIŚNIOWSKA-KIELIAN

EFFECT OF DREDGED BOTTOM SEDIMENT ADDITION TO THE SUBSTRATUM ON THE FODDER VALUE OF PLANT MATERIAL

Part 2. QUANTITATIVE RATIOS BETWEEN MACROELEMENTS

WPŁYW DODATKU BAGROWANEGO OSADU DENNEGO DO PODŁOŻA NA WARTOŚĆ PASZOWĄ MATERIAŁU ROŚLINNEGO

Cz. 2. STOSUNKI ILOŚCIOWE MIĘDZY MAKROELEMENTAMI

Abstract: Pot experiments were conducted in 2004 and 2005 on substrata prepared from soil and quartz sand together with bottom sediment dredged from the Roznow Reservoir. The investigations aimed at an assessment of increasing supplements of the bottom sediment to the substratum on the quality of cultivated plant biomass. The assessment criteria were values of quantitative ratios between macroelements in the biomass. Assessed were weight Ca:Mg and Ca:P ratios and K:Na and K:(Ca+Mg) ionic ratios.

Values of Ca:P ratio in the unicotyledonous plants from the control objects were too low, whereas in the dicotyledonous too high. The sediment supplement considerably widened this ratio but generally worsened the quality of obtained biomass. With growing proportion of the sediment in the substratum a widening of Ca:Mg weight ratio was observed and narrowing of K:(Ca+Mg) ionic ratio, which worsened the biomass quality. Only in case of barley cultivated in the second year of the experiment a positive effect of the sediment on the analyzed indices of fodder quality was observed. K:Na ratio in biomass of all plants was too wide and the sediment added to the substratum improved this parameter value. Greater changes of the analyzed ratios value were registered in the plants growing on substrata with sand as compared with the substrata based on light soil. A stronger influence of the bottom sediment on shaping quantitative interrelations between the analyzed macroelements was found in the dicotyledonous than in the unicotyledonous.

Bottom sediment affects shaping quantitative ratios between elements in plant biomass in a similar way as liming, therefore agricultural application of dredged sediment as a deacidifying material is possible, however worsening of some indices of plant fodder value should be taken into consideration.

Keywords: bottom sediment, relationships between macroelements, fodder value

Technical degradation of dam reservoirs has been currently the most important problem in their operation. Their silting results in limited possibilities of a hydroelectric

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[1] Department of Agricultural Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone +48 12 662 4347, fax +48 12 662 4341, email: niemiecm@tlen.pl

plant operation and in future may cause problems with potable water supply for many cities [1]. Dredging of dam reservoirs is the only efficient method to recover their primary functions [2]. Therefore, in future it will be necessary to remove the sediments from reservoir regardless of the costs of such endeavours [3]. In Poland most areas are susceptible to erosion which entails more rapid silting of dam reservoirs. The Roznow Reservoir is the fastest silting dam reservoir in Poland and after 50 years of its operation its length decreased by 40 %. Reclamation measures are crucial for prolonging operation time of this reservoir [4]. Dredging produces a great mass of sediment which should be managed. Bottom sediments are the main link in matter cycling in the water ecosystem providing a reservoir of many elements, which were periodically inactivated [5]. A partial dredging of the Roznow Reservoir started in 2003. The removed sediment was stored on the lagoons formed from a part of the reservoir bowl [6]. Such method of sediment utilization diminished the reservoir area and makes impossible its total reclamation. Bottom sediment excavated during dredging usually have alkaline reaction and large content of fraction of silt and clay, therefore they may reveal similar effect as waste rocks [7], so they may be regarded a valuable material for improving light acid soils properties.

The experiments aimed at an assessment of potential management of the dredged bottom sediment in agriculture. The assessment criterion was fodder value of plant biomass obtained on the substrata to which the sediment supplements were added. The plant material was evaluated on the basis of reciprocal quantitative relations between macroelements in the biomass.

Material and methods

The pot experiments were conducted in 2004–2005 on the substratum composed of light soil or quartz sand, to which bottom sediment dredged from the Roznow Reservoir was added (Table 1).

Table 1

Selected properties of substrata components used in experiments

Component	pH_{KCl}	P	Mg	Ca	Na	K	P	K_2O
		total content [$g \cdot kg^{-1}$]					available forms [$mg \cdot kg^{-1}$]	
Sediment	7.2	0.532	3.833	17.46	0.973	8.632	18.0	96.6
Soil	5.82	0.392	0.564	1.038	0.084	0.556	63.3	256
Sand	6.39	0.072	0.824	0.417	0.091	0.459	4.45	19.2

The experimental design comprised 11 combinations of substrata in three replications. The sediment share in the substratum was increasing from 10 to 100 %, regularly by 10 % on the subsequent treatments. The control objects were soil and sand without the sediment admixture. Basic fertilization of 1 g N, 0.25 g P and 1.25 g K per pot was applied for all treatments and thoroughly mixed with the substratum. Chemically pure

NH_4NO_3, KH_2PO_4 and KCl were used. The test plants were maize (*Zea mays* L.), ‘Prosna’ F1 c.v., and horse bean (*Vicia faba* L.), ‘Nadwislański’ c.v., as a consecutive plant, and oat (*Avena sativa* L.), ‘Chwat’ c.v., and narrowleafed lupine (*Lupinus angustifolius* L.), ‘Sonet’ c.v., as a consecutive plant. In the experiments continued on the same substrata in 2005 spring barley (*Hordeum vulgare* L.), ‘Rambo’ c.v., was cultivated as the test plant. After harvest the plant material was dried, the samples were dry mineralized and macroelements were assessed after the ash dissolving in HNO_3 (1:2) using ICP-AES method. On the basis of macroelement contents in the aerial plant biomass Ca:P and Ca:Mg weight ratios were computed, as well as K:Na and K:(Ca+Mg) ionic ratio.

Results and discussion

An assessment of plant fodder value on the basis of their chemical composition does not provide full information about their ability to meet animal nutritional needs for micro- and macroelements. At plant utilization for feeds the quantitative relations between the elements are often more important criterion of their usability than the contents of individual elements in the biomass. Too high content of one element may synergistically or antagonistically affect the other components causing their limited or excessive absorption by animal organisms. The proper ratio between elements in feed affects their bioavailability and thus the healthiness and productivity of animals [8]. Wrong proportions between the nutrients may also negatively affect plant growth and development. Too high calcium content in the substratum causes reduced uptake of phosphorus, magnesium and most other microelements, which leads to so-called apparent element starvation. In order to assess fodder value of the plants obtained in the experiment the most important ionic and weight ratios were computed between the macroelements in their biomass.

Ca:P weight ratio in the obtained plants ranged from 0.93 to 22.0 (Table 2).

Lupine revealed the widest, while barley the narrowest calcium to phosphorus ratio. The lowest values of this parameter were observed in all control plants growing in the soil and sand. A 10 % admixture of the sediment to the substratum already caused several-fold widening of this ratio in plants cultivated first. In legumes biomass cultivated as consecutive plants, this parameter value widened to a lesser degree. In the second year of the experiment less than twofold widening of Ca:P weight ratio was registered in barley biomass under the influence of the smallest sediment supplement. Bigger admixtures of the sediment to the substratum did not cause any more changes of this parameter value, except for the legumes in which further widening was observed at the sediment admixture reaching up to 30 % of the substratum mass. Generally higher values of this parameter were assessed in the plants grown on substrata with sand than with soil.

The largest diversification of Ca:P ratio (RSD %) in biomass of plant grown on substrata with soil was observed for lupine and on substrata with sand for horse bean and the smallest one on both kinds of substrata was found for barley.

Table 2

Values of weight calcium : phosphorus ratio (Ca:P) in plant biomass

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	Ca:P									
0	0.95	1.62	3.07	4.64	1.24	1.37	0.93	2.67	4.17	1.34
10	4.19	3.59	6.54	6.24	2.15	4.77	3.35	9.59	11.94	2.25
20	4.50	3.65	9.72	16.72	2.61	4.97	3.22	12.38	12.98	2.63
30	3.82	2.67	9.08	13.42	2.38	4.50	2.69	11.79	18.68	2.49
40	4.85	2.61	9.48	10.50	2.26	5.16	2.98	10.95	16.73	1.94
50	4.97	2.71	10.19	21.46	1.76	4.98	3.12	11.00	17.76	2.01
60	4.34	2.25	12.06	18.81	2.47	4.85	3.38	6.73	13.73	2.56
70	5.12	2.82	12.66	18.32	2.13	5.33	4.05	5.04	15.46	2.00
80	4.56	3.16	15.06	16.41	2.42	4.89	2.41	6.34	16.83	2.58
90	4.76	1.97	11.89	22.01	2.24	4.65	2.36	2.37	14.75	2.35
100	4.75	2.96	10.47	18.75	2.76	4.75	2.96	10.47	18.75	2.76
Mean	4.26	2.73	10.02	15.21	2.22	4.57	2.86	8.12	14.71	2.26
SD	1.16	0.62	3.19	5.85	0.42	1.08	0.80	3.65	4.16	0.41
RSD	27.19	22.86	31.86	38.44	18.89	23.75	27.88	44.90	28.30	18.31

Explanation for Tables 2–5: SD – standard deviation, RSD – relative standard deviation [%].

The optimal Ca:P ratio is 2:1 [9]. Even the smallest addition of the sediment to the substratum exceeded the recommended value for all plants, except barley cultivated in the second year of the experiments, in which it was observed that C:P ratio remained on a level approximate to optimal at each sediment supplement to the substratum. Value of Ca:P weight ratio in the analyzed plants was changing apparently under the influence of bottom sediment admixture to the substratum. In research conducted by Wyszkowski [10] mean values of this parameter in barley and oat biomass at the flowering stage were 0.89 and 0.59, respectively. These values were slightly lower than in plants on the control objects in the presented experiments. Ca:P weight ratio in horse bean leaves and straw assessed in Wyszkowska's investigations [11] reached values within the range of 10–15, whereas this ratio value in horse bean straw oscillated around 10 [12]. In the research conducted by Traba et al [13] the value of Ca:P ratio in legumes gathered from meadow sward of the San River valley and Dynowskie Highland fluctuated from 5 to 10. Kochanowska and Nowak [14] estimated that values of this ratio in meadow hay ranges from 1.3 to 2.7. Labuda et al [15] registered widening of Ca:P ratio to 2.4 in oat biomass at panicle appearance stage under the influence of liming, whereas this ratio value in the control plants in their experiment was 1.9. The values of weight ratios from the control objects obtained in the Author's own experiments were approximate to literature data, however at increased share of the sediment in the substratum their interrelations were widening, reaching considerably higher values than considered optimum for plants designed for feeds. The main factor generating changes of Ca:P weight ratios in maize and oat biomass was phosphorus content in these plants. In effect of the sediment admixture to the substratum phosphorus uptake by the plants decreased considerably, reaching much lower values than optimum in fodder plants [9]. In horse bean and lupine biomass increased calcium accumulation was observed simultaneously to decreasing phosphorus value.

Ca:Mg weight ratio in plant biomass produced on all experimental treatments ranged from 2.21 to 16.64 (Table 3).

Table 3

Values of weight calcium : magnesium ratio (Ca:Mg) in plant biomass

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	Ca:Mg									
0	2.75	5.61	9.02	10.57	5.35	2.33	2.60	8.84	6.54	4.59
10	2.99	7.68	12.42	6.97	6.80	2.88	6.71	12.48	13.05	5.05
20	2.91	6.40	13.32	15.14	6.27	2.67	6.99	12.62	14.17	8.02
30	2.40	5.08	12.10	12.98	4.65	2.68	5.82	13.26	16.64	5.39
40	2.72	4.85	13.13	7.74	4.56	2.82	5.22	10.91	11.22	4.42
50	2.73	4.45	10.11	13.97	3.19	2.68	6.34	10.49	13.16	3.73
60	2.51	4.98	11.84	12.41	3.53	2.67	6.39	8.26	12.36	4.01
70	2.43	4.64	10.17	14.23	3.44	2.50	6.36	6.63	12.46	3.45
80	2.80	4.81	10.82	13.31	3.33	2.22	5.16	7.76	12.77	3.30
90	2.33	3.60	11.51	14.14	2.95	2.37	5.54	7.87	12.68	3.08
100	2.21	5.33	9.39	13.36	3.46	2.21	5.33	9.39	13.36	3.46
Mean	2.62	5.22	11.26	12.26	4.32	2.55	5.68	9.86	12.58	4.41
SD	0.25	1.07	1.46	2.70	1.32	0.23	1.20	2.24	2.42	1.41
RSD	9.68	20.58	13.00	22.01	30.57	9.22	21.07	22.71	19.24	31.98

Mean value of this parameter in all plant biomass was 7.08. The highest values of Ca:Mg ratio were registered in horse bean and lupine, while the lowest in maize. In the response to a 10–20 % sediment addition to the substratum a widening of Ca:Mg ratio in all plant biomass happened, except for lupine cultivated on the substrata with soil. Higher supplements of the sediment resulted in narrowing of this ratio and in plants cultivated in the sediment itself it was as a rule lower than observed in the control plants. The exception were oat and lupine on substrata prepared on the basis of sand, where a considerable widening of Ca:Mg ratio was observed under the influence of the sediment addition to the substratum.

The largest diversification of Ca:Mg ratio (RSD %) in biomass of plant grown on both kinds of substrata was observed for barley and the smallest one for maize.

Optimum Ca:Mg ratio in good quality feeds is 3:1 [16]. Bottom sediment supplement constituting 20–30 % of the substratum mass generally worsened the quality of the obtained plants assessed according to fodder usability criteria, whereas bigger supplements of the sediment improved the quantitative interrelations between calcium and magnesium. Values of Ca:Mg weight ratios were changing to a lesser degree than Ca:P ratio because of usually observed positive relationship between the contents of both elements, which was a consequence of their high concentrations in the sediment. In research conducted by Brogowski et al [18] the value of this ratio in barley biomass at shooting stage was about 2. In legumes gathered from the meadow sward in the San River valley the ratio assumed the value about 3.5 [13]. In horse bean straw the mutual ratios of these elements reached the value of 15 [12]. It might have been caused by a decrease in magnesium content in all plants, except for maize, as well as considerable increase in calcium content. Gorlach and Curylo [19] obtained similar results; the same authors observed widening of Ca:Mg ratio in maize biomass from 1.6 in the control plants to 2.44 after application of calcium in the amount equal to the value of 2 hydrolytic acidity. High values of Ca:Mg ratio were caused by a very small magnesium content in the plants from these experiments. Too high values of Ca:Mg ratio may cause hypercalcemia in animals, which is seen as a apparent starvation of other elements [16].

K:Na ionic ratio fluctuated between 4 and 192 and mean for all plants was 55 (Table 4).

Table 4

Values of ionic potassium : sodium ratio (K:Na) in plant biomass

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	K:Na									
0	111	45	88	26	58	130	30	104	33	50
10	185	25	30	25	61	142	34	39	42	42
20	141	37	27	34	58	181	35	27	30	43
30	173	42	17	25	61	152	37	9	25	36
40	173	31	8.7	17	43	191	37	25	26	62
50	125	37	7.5	13	45	143	13	20	17	48
60	135	35	4.0	20	43	177	13	15	17	38
70	192	32	6.2	14	42	129	12	3.6	16	26
80	174	42	5.5	33	47	159	24	8.3	16	37
90	154	29	3.6	21	41	121	20	5.6	19	36
100	150	23	7.6	24	44	150	23	7.6	24	44
Mean	155.7	34.4	18.7	22.9	49.4	152.3	25.3	24.0	24.1	42.0
SD	25.9	7.1	24.8	6.9	8.2	22.8	9.9	28.7	8.4	9.4
RSD	16.7	20.7	132.7	29.9	16.7	15.0	39.2	119.5	34.7	22.3

Bottom sediment supplement constituting 10 % of the substratum mass caused considerable widening of K:Na ratio in maize biomass but narrowing of its value in horse bean. In biomass of the other plants this ratio value changed only slightly. Further increase in the sediment share in the substrata caused a systematical lowering of K:Na ionic ratio value in oat, horse bean and barley. The share of both elements depended to a greater degree on the amount of added sediment than on the other component of the substratum used in the experiments.

Value of K:Na ionic ratio in plant biomass cultivated in the presented experiments revealed very high changeability depending on the plant species and conditions of the substratum generated by the share of bottom sediment in the substratum. The largest diversification of K:Na ratio (RSD %) in biomass of plant grown on both kinds of substrata was observed for horse bean and the smallest one for maize.

The optimum potassium to sodium ratio amounts to 5–8:1 [9, 16]. The sediment addition to the substrata, based both on soil and sand caused a worsening of interrelations between potassium and sodium only in maize biomass. In the other plants, improved biomass quality was observed assessed on the basis of this parameter [9, 16].

In conditions of variable nitrogen fertilization the values of this parameter in maize ranged from 16 to 24 [17]. These values were almost 10-fold lower than observed in maize biomass in the presented experiment. Wyszkowski [10] found that values of K:Na ionic ratios in spring barley biomass were 108 and in oat 193. These relations between the elements are approximate to registered in lupine, oat and maize biomass in presented Authors' own experiments. Research conducted by Czapla and Nowak [17] shows that value of this ratio in oat biomass at the flowering stage was 5.5 and in barley biomass at the shooting stage reached 6.4 [18]. Shtangeeva and Ayrault [20] report that the values of K:Na ratio in wheat biomass approximated 33.9. As may be seen, the literature data indicate a considerable changeability of potassium and sodium interrelations in plants depending on soil properties and plant species. The value of this ratio in horse bean straw registered in research of Nowak et al [12] was 28. In biomass of lupine, oat and barley obtained in the Author's own research values of this ratio were twice higher than in the experiments of Czapla and Nowak [17]. Value of K:Na ionic ratio in the test plants depended primarily on sodium content changing under the influence of increasing sediment supplements. Changing sodium concentrations in plant biomass caused fluctuations in the value of K:Na ratio, but they were so small that had no greater influence on the plant biomass quality.

The value of K:(Ca+Mg) ionic ratio in plant biomass ranged from 0.24–2.7 (Table 5).

The highest value of K:(Ca+Mg) ratio was assessed in barley and the lowest in horse bean biomass. The largest diversification of this ratio (RSD %) in biomass of plant grown on the substrata with soil was registered for lupine and the smallest one for barley. In biomass of plant grown on the substrata with sand the largest diversification of K:(Ca+Mg) ratio was noted for oat and the smallest one for maize.

A 10 % sediment supplement to the substrata generally led to narrowing of this ratio in plant biomass, except for lupine cultivated on substrata with soil. Bigger admixtures usually did not change its value. The sediment share in the substratum had a greater effect on this parameter value than the kind of the second component. Its changes were the most affected by the changes in calcium and potassium concentrations, whereas magnesium content proved to be less important.

Table 5

Values of ionic potassium : (calcium + magnesium) ratio [K:(Ca+Mg)] in plant biomass

Share of sediment in substratum [%]	Substratum with soil					Substratum with sand				
	maize	oat	horse bean	lupine	barley	maize	oat	horse bean	lupine	barley
	K:(Ca+Mg)									
0	1.09	0.94	0.51	0.60	2.14	1.42	2.12	0.41	1.17	2.70
10	1.08	0.62	0.37	1.27	1.95	0.89	0.87	0.36	0.68	1.72
20	0.91	0.73	0.36	0.45	1.83	0.96	0.78	0.35	0.59	1.64
30	0.99	1.03	0.33	0.58	1.89	0.94	0.89	0.32	0.48	1.64
40	0.86	0.92	0.31	0.81	1.77	0.87	0.85	0.31	0.61	1.93
50	0.84	0.89	0.42	0.50	2.10	0.89	0.64	0.29	0.51	2.00
60	0.85	1.00	0.28	0.42	1.81	1.01	0.65	0.40	0.56	1.52
70	0.92	0.77	0.36	0.45	2.13	0.89	0.54	0.24	0.55	1.91
80	0.92	1.06	0.31	0.46	2.09	1.00	0.88	0.56	0.54	2.01
90	0.93	1.18	0.34	0.42	1.86	0.96	0.91	0.47	0.54	1.76
100	0.97	0.92	0.44	0.40	1.81	0.97	0.92	0.44	0.40	1.81
Mean	0.94	0.91	0.37	0.58	1.94	0.98	0.91	0.38	0.60	1.88
SD	0.08	0.16	0.07	0.26	0.14	0.15	0.42	0.09	0.20	0.32
RSD	8.99	17.47	18.28	44.69	7.42	15.57	45.98	24.12	33.40	16.83

The optimal K:(Ca+Mg) ratio is 2:1 [16]. In all plants worsening of plant biomass assessed considering this parameter was observed after the bottom sediment application. Value of K:(Ca+Mg) ionic ratio in plants is very important when they are used for feeds because its too high value, which is a consequence of luxury potassium uptake by plants, may lead to hypomagnesemic tetany in cattle. Falkowski et al [9] found that pasture tetanus may occur when this ratio value exceeds 2.5. Ionic ratio between potassium content and the sum of calcium and magnesium in plants in the presented experiments was generally lower than its critical value and in most cases it was below 1. Kaczor [21] observed similar values in orchardgrass on unlimed treatments, whereas liming led to narrowing of this ratio.

In Wyszkowski's research [22], value of this ratio in barley biomass at the flowering stage ranged from 1.95 to 2.35, whereas in oat at the same development stage the ratio assumed values of 2.05–2.35. Generally, these values are several times higher than observed in the Author's own investigations. Wyszkowska [11] found the value of this ratio in horse bean straw slightly over 2.5. Malinska i Pietrasz-Kesik found that K:(Ca+Mg) ratio in maize biomass is 1.25. The main factor modifying this ratio value in plant biomass obtained from the Authors' own experiments was calcium content, the level of which in most cases was increasing after the application of a 10 % bottom sediment admixture to the substratum. Greater changes appeared on the substrata with sand because the plants responded by a higher increase in calcium content in the biomass than the substrata with soil.

Bottom sediment applied as an admixture to soil supplied considerable amounts of calcium which neutralized the substratum. Observed changes of quantity relations between the analyzed elements are similar to assessed after liming [15, 19, 21]. Therefore it may be supposed that agricultural management of dredged bottom sediment as a deacidifying material is possible, however, worsening of some quality indices of the material designed for fodder should be taken into consideration.

Conclusions

1. Bottom sediment dredged from the Roznow Reservoir added to the substratum caused considerable changes of the value of quantitative relations, particularly Ca:P and K:Na.
2. Bottom sediment supplement to the substratum worsened values of Ca:P and Ca:Mg weight ratios and the value of K:(Ca+Mg) ionic ratio in the first year of the experiment.
3. An improvement of K:(Ca+Mg) ionic ratio was observed as an effect of bottom sediment application in the first year of the experiments.
4. Shaping of weight ratios between the macroelement was affected most by increasing calcium and sodium contents in biomass and considerably reduced phosphorus uptake.
5. An admixture of bottom sediment to the substratum generally worsened quantitative relations between the investigated elements in the first year of the experiment, however it improved the quality of barley biomass cultivated on the same substrata in the second year of the experiments.
6. Dredged bottom sediment affects the quantity relations between the elements in plant biomass in a similar way as liming, therefore the use of this sediment in agriculture is possible as a deacidifying material, however, worsening of some indices of plant fodder quality should be taken into consideration.

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WPŁYW DODATKU BAGROWANEGO OSADU DENNEGO DO PODŁOŻA NA WARTOŚĆ PASZOWĄ MATERIAŁU ROŚLINNEGO

Cz. 2. STOSUNKI ILOŚCIOWE MIĘDZY MAKROELEMENTAMI

Katedra Chemii Rolnej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: W 2004 i 2005 r. przeprowadzono doświadczenia wazonowe, w których jako podłoża użyto glebę lekką i piasek kwarcowy oraz bagrowany osad denny ze Zbiornika Rożnowskiego. Celem badań była ocena wpływu wzrastających dodatków osadu dennego do podłoża na jakość biomasy uprawianych roślin. Jako kryterium oceny przyjęto wartości stosunków ilościowych między makroelementami w biomasie. Oceniono stosunki masowe Ca:Mg i Ca:P oraz stosunki jonowe K:Na i K:(Ca+Mg).

Wartości stosunku Ca:P w roślinach jednoliściennych z obiektów kontrolnych były zbyt małe, a w roślinach dwuliściennych zbyt duże. Dodatek osadu znacznie rozszerzał ten stosunek, pogarszając na ogół jakość uzyskanej biomasy. W miarę wzrostu udziału osadu w podłożu obserwowano rozszerzenie stosunku masowego Ca:Mg oraz zawężanie stosunku jonowego K:(Ca+Mg), co pogarszało jakość biomasy. Tylko w przypadku jęczmienia uprawianego w drugim roku doświadczeń stwierdzono dodatni wpływ dodatku osadu na kształtowanie się badanych wskaźników jakości paszy. Stosunek K:Na w biomasie wszystkich roślin był zbyt szeroki, a osad dodawany do podłoża poprawiał wartość tego parametru. Pod wpływem dodatku osadu dennego zaobserwowano większe zmiany wartości badanych stosunków w roślinach rosnących na podłożach z piaskiem w porównaniu z podłożami sporządzonymi z gleby lekkiej. Stwierdzono większy wpływ osadu dennego na kształtowanie się wzajemnych stosunków ilościowych pomiędzy badanymi makroelementami w roślinach dwuliściennych niż jednoliściennych.

Osad denny oddziałuje na kształtowanie stosunków ilościowych pomiędzy pierwiastkami w biomasie roślin podobnie jak wapnowania, jest więc możliwe rolnicze wykorzystanie bagrowanego osadu dennego jako materiału odkwaszającego, licząc się z pogorszeniem się niektórych wskaźników wartości paszowej roślin.

Słowa kluczowe: osad denny, stosunki między makroelementami, wartość paszowa

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Iwona RADKOWSKA[1] and Adam RADKOWSKI[2]

NUTRITIVE VALUE OF MEADOW SWARD SILAGES DEPENDING ON THE TYPE OF FERTILIZATION

WARTOŚĆ POKARMOWA KISZONEK Z RUNI ŁĄKOWEJ W ZALEŻNOŚCI OD RODZAJU NAWOŻENIA

Summary: The aim of the conducted studies was an estimation of the quality and nutritive value of silages derived from the meadow sward as affected by the kind of fertilization used. The following variants were taken into account: the control object without fertilization, NPK mineral fertilization, fertilization with manure and fertilization with liquid manure.

The conducted fertilization resulted in the significant growth of the mean organic matter and total protein content, what in turn influenced the higher nutritive value expressed as UFL, UVF, PDIN and PDIE in comparison to the non-fertilized object. Treatment with natural fertilizers affected the increased level of organic matter and total protein by 4 and 21 %, respectively when compared with the respective values found for the silages derived from the control object. Furthermore, the increment of nutritive value amounted to 13 % – UFL, 17 % – UVF, 13 % – PDIN and 11 % – PDIE. In that light, it can be stated that organic fertilization contributes in the increase of the silage quality. The highest growth of the total protein content was observed in the silage derived from the manure fertilized object. On the basis of this observation, it can be stated that properly chosen organic fertilization helps to achieve high quality silages.

Keywords: fertilization, silages, quality and nutritive value

The period of winter feeding in Poland lasts for about 200 days. Thus the production of preserved forages is necessary, which enable the uniform and fully-valuable animal feeding during the whole year [1, 2]. In many farms, because of the necessity of the reduction of costs and because of the high nutritive value, pasture forages constitute a basis of the summer feeding of cows. Above 70 % of the yield from the permanent grasslands is collected in the form of hay and pasture green forage, but only 5 % of this is ensilaged. This phenomenon is disadvantageous, because when compared with hay

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[1] National Research Institute of Animal Production Balice, ul. Krakowska 1, 32–083 Balice, Poland, phone 666 08 11 49, email: iradkowska@izoo.krakow.pl

[2] Department of Grassland, Agricultural University of Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone 012 662 43 61, fax 012 633 62 45, email: rrradkow@cyf-kr.edu.pl

silage is characterized with lower level of losses of the nutrients and at the same time higher nutritive value [3]. Silages are fully-valuable and the cheapest forages in the winter feeding of ruminants, especially in the case of simplified feeding systems [4, 5]. The quality of the silage is determined by many chemical and physical parameters. The most important are: the content of saccharides and buffering substances, the dry matter level, soil structure and pollutions [6, 7]. Many of this factors is influenced by the kind of utilized fertilization, especially nitrogen, which negatively affects the ensilage process.

The aim and scope of the study

The aim of the study was to evaluate the quality of the obtained silage in term of the utilized fertilization system. The estimation comprised mainly the determination of the effect of the applied fertilization on the level of collected nutrients in the silage. Three kinds of fertilization were applied to accomplish the goal. Four variant were taken into account in the experiment, ie:

Variant 1 – the control object, the silage derived from the non-fertilized sward,
Variant 2 – the silage derived from the minerally fertilized object – NPK,
Variant 3 – the silage derived from the object fertilized with manure,
Variant 4 – the silage derived from the object fertilized with liquid manure.

Materials and methods

The field experiment was conducted in the years 2006–2008 in the private, individual farm in Solca, in the Gmina Pilica administrative district, within Zawiercie County, Silesia province, located on the altitude of 320 m. One-factor experiment was located on the brown, acidic soil (pH_{KCl} amounted to 5.2) of a V quality class. The soil contained medium level of assimilable potassium, manganese and zinc and was poor in assimilable phosphorus and copper.

During the vegetation period (April–September) the average rainfall amounted to 338.1; 375.4 and 320.3 mm, respectively in the year 2006, 2007 and 2008, whereas average air temperatures reached the values of 15.2; 14.3 and 14.9 ^{o}C, respectively.

The kind of fertilization was a determining factor in the study. In the fertilization of the meadow in the variant with the mineral fertilization the following fertilization was used: after the first regrowth – 80 kg N $\cdot$ ha^{-1} and after the II regrowth – 60 kg N $\cdot$ ha^{-1} in the form of ammonium saltpetre, phosphorus once in the spring in the amount of 120 kg P_2O_5 $\cdot$ ha^{-1} as a triple superphosphate and potassium after the first and second regrowth – 60 kg K_2O $\cdot$ ha^{-1} for each regrowth as 57 % potassium salt. In the variant fertilized with manure the cattle manure in a dose of 25 Mg $\cdot$ ha^{-1} was applied in the early spring. The content of chemical components in manure was as follows: dry matter – 24.2 %; total N – 0.52 %; P – 0.15 %; K – 0.57 %; Ca – 0.28 %; Mg – 0.08 and Na – 0.07 %.

In a 25 Mg of manure the following levels of components were derived: total N – 130 kg, P – 38 kg, K – 143 kg, Ca – 70 kg, Mg – 20 kg and Na – 18 kg.

As it come to the variant fertilized with liquid manure, the cattle liquid manure in an amount of 20 $m^3 \cdot ha^{-1}$ was applied, which was divided on a two equal doses for a first and second regrowth. Liquid manure contained: dry matter – 6.7 %; total N – 0.66 %; P – 0.14 %; K – 0.27 %; Ca – 0.24 %; Mg – 0.11 % and Na – 0.08 %. Thus with a dose 10 m^3 of liquid manure the following amounts of components were provided: total N – 66 kg, P – 14 kg, K – 27 kg, Ca – 24 kg, Mg – 11 kg and Na – 8 kg.

The area of each field amounted to 500 m^2. The silages were derived from the first swath of the meadow flora. The plant material was collected in two stages, the first included mowing of the plants at the turn of earing and flowering stage of grasses with a rotary mower, than the green fodder was slightly dried by one-time turning it over. The fodder was raked 30 minutes before picking up. The material was collected using constant-chamber baler, then it was transported to the storage place and wrapped using bale wrapper. The average time from the bale forming to its wrapping with foil did not exceed 4 hours.

Before grazing the samples of silages were collected for the chemical analysis, which comprise the determination of the fundamental components by the Weenden method [8], pH using pH-meter, the ammonium level by the Conway method [9].

The content of organic acids was evaluated using the Varian 3400 type gas chromatograph. The nutritive value was evaluated in the INRA 1988 units using Winwar 1.6 software (DJG). The estimation was done on the basis of tabular coefficients of forage distribution in the rumen and intestines. The obtained results were subjected to the analysis of variance, and the significance of differences was estimated on the basis of Duncan test at the significance level of $\alpha = 0.05$.

Results and discussion

The estimation of the quality and real nutritive value of the silages is basic for the proper utilization of these material in the cattle feeding. The complex evaluation of the silage quality includes the determination of:

– chemical factors of quality, which describe the correctness of the fermentation proceeding and are important indicators of the chemical characteristic of the silage quality (pH, lactic, acetic, butyric and valeric acid, the share of $N\text{-}NH_3$ in relation to the total protein, NDF, ADF, ADL),

– the nutritive value expressed in the feed unit for lactation (UFL) or meet production unit (UVF) and the content of the protein digested in the intestines [10].

The chemical characteristic of the silage quality includes the estimation of the fundamental chemical composition (what enables the estimation of the silage nutritive value). The knowledge of the content of structural carbohydrates (NDF, ADF and ADL) is also very important in the evaluation of the silage quality [11].

The study revealed the impact of the applied fertilization on the content of organic components and nutritive value of the meadow sward (Table 1). The concentration of the particular components in silages was diversified and affected by the kind of fertilization used. Utilized in the investigation fertilization had various effect on the content of selected components. Among all examined components the highest diversification was found for the level of total protein (V = 21.7 %), and its content ranged from 7.40 to 11.40 g · kg^{-1}. Mineral fertilization and treatment with manure affected a significant growth of the organic mass content when compared with the control object – the differences amounted to respectively 10 and 8 %. Fertilization with minerals, manure and liquid manure resulted in the significant decrease of the crude fiber in silages derived from the meadow sward (by 10, 8 and 4 %) in relation to the control object. As a result of mineral fertilization and application of manure a significant increase of the raw fat content was determined, which concentration raised by 9 and 6 % in comparison with the silage prepared from the meadow sward collected from the non-fertilized object. In the case of the object fertilized with liquid manure a 10 % decrease in the concentration of this component was noticed.

Table 1

The chemical composition of the silages as affected by the fertilization kind
(means for three years)

Specification	Variant			
	Control	Mineral fertilization	Manure	Liquid manure
pH	6.04 a*	6.03 a	6.16 ab	6.49 b
[g · kg^{-1} dry matter]				
Organic matter	74.0 a	81.9 b	80.4 b	74.0 a
Total protein	74.0 a	110.0 b	114.0 b	79.7 ab
Crude fiber	389.5 b	349.6 a	357.4 ab	373.2 b
Raw fat	28.5 a	31.2 b	30.3 b	25.8 a
Non-nitrogen extract	434.1 ab	427.3 a	417.8 a	447.4 b
ADF	445.3 b	409.0 a	405.5 a	451.8 b
ADL	59.0 a	67.4 b	56.1 a	77.3 b
NDF	705.6 b	645.0 a	642.6 a	680.3 b
Lactic acid	2.34 a	4.98 b	6.63 c	2.85 a
Acetic acid	9.80 b	8.66 ab	7.85 a	9.10 b
Content of N-NH_3 in total N [%]	0.039 a	0.054 ab	0.078 b	0.047 ab
UFL [kg^{-1} d.m.]	0.647 a	0.744 b	0.748 b	0.749 b
UVF [kg^{-1} d.m.]	0.547 a	0.658 b	0.664 b	0.665 b
PDIN [kg^{-1} d.m.]	49 a	73 b	78 b	51 a
PDIE [kg^{-1} d.m.]	67 a	81 b	81 b	71 ab

* Means marked with the same letter are not statistically different following verification with the Duncan test ($p = 0.05$); ADF – acid detergent fiber, ADL – acid detergent lignin and NDF – neutral detergent fiber; UFL – Feed Unit for Lactation, UVF – Meat production Unit, PDIE – protein digested in the small intestine supplied by rumen-undegraded dietary protein plus protein digested in the small intestine supplied by microbial protein from rumen-fermented organic matter, PDIN – protein digested in the small intestine supplied by rumen-undegraded dietary protein plus protein digested in the small intestine supplied by microbial protein from rumen-degraded protein.

As it was mentioned before, the knowledge of the content of structural carbohydrates (NDF, ADF and ADL) is of a great importance in the evaluation of the silage quality. As a result of the mineral fertilization and fertilization with manure significant reduction in the content of the ADF (*acid detergent fiber*) fraction was observed, which amounted to 8 and 9 %, respectively, in relation to the non-fertilized object. The concentration of the ADL (*acid detergent lignin*) decreased only in the object fertilized with manure (5 % in relation to the control object). On the other hand, the content of NDF (*neutral detergent fiber*) was 9.9 and 4 % lower in the objects treated with mineral fertilizer, manure and liquid manure than the NDF level in the control field.

The pH value, the concentration of the organic acids, the share of ammoniacal nitrogen in the total nitrogen content are among the most important factors characterizing the proceeding of the fermentation processes [3]. The silage acidity (pH) indicates the intensity of the fermentation processes [12]. The pH level in the examined silages fluctuated in the range of 6.03–6.49 in dependence on the fertilization variant.

The content of organic acids formed during the ensilage process was diversified. In this experiment the content of lactic acid ranged from 2.34 to 6.63 $g \cdot kg^{-1}$ dry matter and was very diversified (V = 47.2 %). The level of acetic acid fluctuated in the range of 7.85–9.80 $g \cdot kg^{-1}$ dry matter (V = 9.2 %). The content of ammoniacal nitrogen in analysed variants was low what indicates good quality of the silages as regards $N\text{-}NH_3$ content in relation to the total nitrogen.

As regards the energetic value the investigated forages were characterized with the similar UFL and UVF values. However, as a consequence of the applied mineral fertilization, manure and liquid manure 14, 13 and 14 % growth of the UFL value in relation to the control object was noticed. The respective differences stated for the UVF level between the fertilized objects and non-fertilized object were equal to 18, 17 and 18 %.

On the contrary, the protein value was more diversified and fluctuated in the range of 49–78 for PDIN (V = 23.7 %) and 67–81 $g \cdot kg^{-1}$ d.m. for PDIE (V = 9.5 %). It was on average 20 % (PDIN) and 13 % (PDIE) higher in the fertilized object than the values determined for the control object.

Conclusions

1. The application of natural fertilizers, especially manure, had a great impact on the chemical composition of the examined silages. The positive effect of fertilization was found in the case of the content of total protein, raw fat, ADF, ADL and NDF fractions of fiber.

2. As regards the nutritive value the studied silages were characterized with similar UFL and UVF values. On the contrary, the protein value was significantly higher under the treatment with manure and mineral fertilizers. The fertilization with liquid manure had lower impact on the nutritive value.

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WARTOŚĆ POKARMOWA KISZONEK Z RUNI ŁĄKOWEJ W ZALEŻNOŚCI OD RODZAJU NAWOŻENIA

[1] Instytut Zootechniki – Państwowy Instytut Badawczy
[2] Katedra Łąkarstwa, Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem podjętych badań było określenie jakości i wartości pokarmowej kiszonek pochodzących z runi łąkowej w zależności od zastosowanego nawożenia. W doświadczeniu przyjęto następujące warianty: obiekt kontrolny bez nawożenia, nawożenie mineralne NPK, nawożenie obornikiem i gnojowicą.

W wyniku zastosowanego nawożenia stwierdzono znaczny wzrost średniej zawartości substancji organicznej i białka ogólnego, co przyczyniło się do wzrostu wartości pokarmowej wyrażonej w wartościach parametrów JPM, JPŻ, BTJN oraz BTJE w porównaniu z obiektem nienawożonym. Nawożenie organiczne spowodowało wzrost zawartości substancji organicznej i białka ogólnego odpowiednio o 4 i 21 % w porównaniu z zawartością w kiszonce pochodzącej z obiektu nienawożonego. Z kolei wartość pokarmowa pod wpływem tego nawożenia wzrosła o 13 % JPM, 17 % JPŻ, 13 % BTJN i 11 % BTJE. Stwierdza się, iż nawożenie organiczne przyczynia się do wzrostu jakości kiszonek. Największy wzrost zawartości białka ogólnego odnotowano w kiszonce pochodzącej z obiektu nawożonego obornikiem. Wobec powyższego można stwierdzić, iż odpowiednio dobrane nawożenie organiczne pozwala osiągnąć kiszonki dobrej jakości.

Słowa kluczowe: nawożenie, kiszonki, jakość i wartość pokarmowa

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Antoni ROGÓŻ[1]

EFFECT OF SOIL PROPERTIES ON LITHIUM PHYTOAVAILABILITY
Part 2. LITHIUM CONTENT IN SOIL AFTER COMPLETION OF MAIZE AND RYE VEGETATION

WPŁYW WŁAŚCIWOŚCI GLEBY NA FITOPRZYSWAJALNOŚĆ LITU
Cz. 2. ZAWARTOŚĆ LITU W GLEBIE PO ZAKOŃCZENIU WEGETACJI KUKURYDZY ORAZ OWSA

Abstract: Soil samples were collected from each series after the end of rye vegetation in order to follow changes which occurred in physical and chemical properties. Increasing doses of organic matter and applied two doses of lithium affected changes of soil physical and chemical properties. Applied doses of lithium and organic matter influenced the values of pH and hydrolytic acidity, organic carbon content and the content of lithium in soil. Metal sequential extraction with solutions of various leaching power: H_2O; 2.5 % CH_3COOH; 0.1 mol $K_2P_4O_7 \cdot dm^{-3}$; 0.1 mol $H_2C_2O_4 \cdot dm^{-3}$ + 0.175 mol $(NH_4)_2C_2O_4 \cdot dm^{-3}$ was used to determine lithium content and its forms in soil. In result of sequential extraction were lithium forms extracted from easily soluble, ie bioavailable, through weakly bound to sorption complex to sparingly soluble and immobilized, therefore unavailable to plants. Lithium content in individual fractions was quite diversified. The factor determining this element level in the analyzed soil was applied lithium dose and increasing doses of organic matter, one of many factors affecting the size of sorption complex. Lithium doses of 10 and 20 mg Li per pot very distinctly affected the amount of lithium extracted using 2.5 % CH_3COOH as F-2 form. In this case a similar dependence occurred as in F-1 fraction. The content of lithium bound to organic matter (F-3), extracted with 0.1 mol $K_2P_4O_7 \cdot dm^{-3}$ ranged from 0.212 to 0.340 mg $Li \cdot kg^{-1}$.The quantity of cation bound to organic matter extracted using 0.1 mol $K_2P_4O_7 \cdot dm^{-3}$ was visibly increasing on treatment with growing lithium doses.

Keywords: lithium forms in soil, sequential extraction, soil properties

Natural content of lithium in soil is diversified, fluctuating from several to many mg $Li \cdot kg^{-1}$. The main factors determining the level of this cation in soil comprise the kind of parent rock, soil forming processes, climate, soil pH, organic matter content, degree of moistening, content of floatable particles and anthropogenic factors [1–6].

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[1] Department of Agricultural Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone +48 12 662 4348, fax +48 12 662 4341, email: rrrogoz@cyf-kr.edu.pl

On the basis of his investigations Rogóż [6] revealed that the content of individual lithium forms obtained with the method of metal sequential extraction was quite diversified depending on the content of floatable particles but to a lesser degree on pH value. He also demonstrated a significant dependency between organic carbon content in the researched soils and lithium contents in water soluble forms and exchangeable non-specifically adsorbed form.

The research was conducted to compare the effect of increasing doses of organic matter on the content and forms of lithium in soil polluted with this metal.

Materials and methods

The pot experiment was set up in 2006 in the design comprising the following combinations:

A. Control treatment:
  1 – soil with natural lithium and organic matter contents,
  2 – soil with a supplement of 10 mg Li · pot^{-1} with natural content of organic matter,
  3 – soil with a supplement of 20 mg Li · pot^{-1} with natural content of organic matter,
B. Treatments with increasing lithium and organic matter supplements (as compost):
  4 – with 10 mg Li · pot^{-1} and 26 g of organic matter,
  5 – with 20 mg Li · pot^{-1} and 26 g of organic matter,
  6 – with 10 mg Li · pot^{-1} and 52 g of organic matter,
  7 – with 20 mg Li · pot^{-1} and 52 g of organic matter,
  8 – with 10 mg Li · pot^{-1} and 78 g of organic matter,
  9 – with 20 mg Li · pot^{-1} and 78 g of organic matter.

Maize (*Zea mays* L.) and rye (*Secale cereale* L.) were cultivated as test plants. After completed vegetation of both plants soil samples were collected from each series. The samples were left in linen bags in rooms with free air movement and when dried they were ground in a porcelain mortar and sifted through a sieve with 1 mm^2 mesh. Detailed method and the course of the experiment were presented in the "Material and methods" section in the 1st part of this paper [7].

Basic physicochemical properties were determined in air-dried soil samples with methods commonly used in agricultural chemistry [8]:

– granulometric composition with Bouyoucose-Casagrande method in Proszynski modification,

– pH with potentiometric method in soil suspension in H_2O and in 1 mol KCl · dm^{-3},

– organic carbon content with Tiurin method,

– hydrolytic acidity with Kappen method,

– lithium forms in the analysed soils were assessed with a method of metal sequential extraction [9] modified by Bogacz [1, 10],

– total lithium content was determined as a sum of extracted fractions from F-1 to F-5 (Fig. 1).

The content of individual lithium forms obtained in result of metal sequential extraction was assessed in an acetylene-air flame with ICP AES method on JP238.

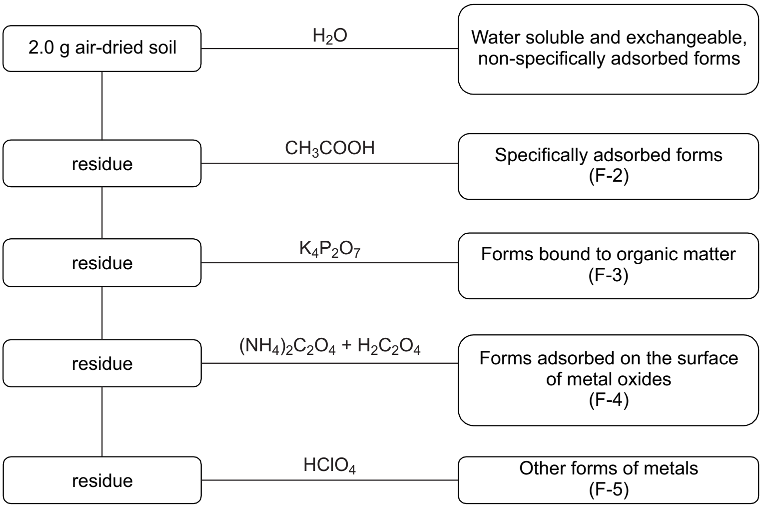

Fig. 1. Scheme of sequential extraction of the lithium fraction in soil [1]

Results and discussion

When rye vegetation was completed soil samples were collected from each series in order to follow changes which occurred in physical and chemical properties. Increasing doses of organic matter and applied two doses of lithium affected changes of soil physical and chemical properties. Applied doses of lithium and organic matter influenced the values of pH and hydrolytic acidity, organic carbon content and the content of lithium in soil after completion of plant vegetation. The soil pH after completed vegetation period assessed in water suspension fluctuated from 5.96 to 6.26, while measured in 1 mol · dm^{-3} KCl from 5.59 to 5.94. Organic C content in the soil used for the experiment was 1.33 %. Increasing doses of organic matter: 26, 52 and 78 g · pot^{-1} caused an increase in organic C. Assuming eg the control treatment with natural content of organic carbon as 100, it may be concluded that applied doses of organic matter 26, 52 and 78 g led to an increase in organic C from 1.5 to 10.4 % (Table 1). These dependencies confirmed the results obtained by Mazur [11].

Lithium content and its forms in soil were determined using metal sequencing extraction with solutions of various leaching power: H_2O; 2.5 % CH_3COOH; 0.1 mol $K_2P_4O_7 \cdot dm^{-3}$; 0.1 mol $H_2C_2O_4 \cdot dm^{-3}$ + 0.175 mol $(NH_4)_2C_2O_4 \cdot dm^{-3}$. In result of sequential extraction were extracted lithium forms from easily soluble, ie bioavailable, through weakly bound to sorption complex to sparingly soluble and immobilized, therefore unavailable to plants. Lithium content in individual fractions was quite diversified. The factor determining this element level in the analyzed soil was the applied lithium dose and increasing doses of organic matter, one of many factors affecting the size of sorption complex.

Table 1

Soil properties after the end of plant vegetation period

Series	Li supplement [mg · pot^{-1}]	Dose of organic matter [g · pot^{-1}]	pH		Hh [mmol(+) · kg^{-1}]	Organic C [g · kg^{-1}]
			H_2O	KCl		
1	0	0	5.96	5.59	22.0	1.505
2	10	0	6.17	5.71	14.2	1.481
3	20	0	6.08	5.65	15.1	1.515
4	10	26	6.18	5.76	11.2	1.567
5	20	26	6.15	5.72	13.8	1.523
6	10	52	6.23	5.94	13.8	1.614
7	20	52	6.26	5.83	21.2	1.615
8	10	78	6.19	5.86	14.7	1.636
9	20	78	5.97	5.90	12.5	1.656

The quantity of lithium extracted using H_2O comprised water soluble fractions present in the soil solution and the non-specifically adsorbed exchangeable form (weakly bound to the soil sorption complex), thus bioavailable to plants. The amount of lithium extracted with H_2O as F-1 form depended on the natural content of this element in soil, lithium dose and the applied dose of organic matter, and ranged from 0.26 mg to 0.98 mg Li · kg^{-1}.

Lithium doses of 10 and 20 mg Li per pot markedly affected the quantity of lithium as F-1 form extracted using H_2O. Assuming lithium content extracted in F-1 form on the control treatment with natural content of this element as 1, it may be seen that lithium amounts extracted with increasing doses, ie 10 and 20 mg Li · pot^{-1} were twice and four fold bigger.

Applied growing doses of organic matter had an inhibitory effect on the quantity of lithium extracted as F-1 form using H_2O. Assuming eg lithium content extracted as F-1 form on the treatment with elevated lithium content (10 mg Li · pot^{-1}) as 100, it may be seen that growing doses of organic matter 26, 52 and 78 g · pot^{-1} caused the decrease of lithium amounts extracted as F-1 fraction by 9, 15 and 2 %, respectively. On the other hand, increasing doses of organic matter in case of 20 mg Li · pot^{-1} addition affected the amount of extracted metal in various directions (Table 2).

On the basis of previous investigations Rogóż [6] revealed that the amount of lithium extracted using 0.05 mol $BaCl_2$ · dm^{-3} fluctuated from 0.020 to 0.370 mg Li · kg^{-1} soil at geometric mean 0.109 mg Li · kg^{-1}, comprising the total of two fractions, ie water soluble and exchangeable, non-specifically adsorbed F-1.

The amounts of lithium in the other fractions extracted by means of the other extractors with various power depended on the natural content of this cation in the soil, applied lithium dose and the dose of organic matter.

This element content extracted with 2.5 % CH_3COOH determined as a form specifically adsorbed by soil colloids F-2 fluctuated from 0.140 to 0.780 mg Li · kg^{-1}.

Table 2

Contents of individual lithium forms after the end of plant vegetation [mg Li $\cdot$ kg^{-1}]

Series	Li addition [mg $\cdot$ pot^{-1}]	Dose of organic matter [g $\cdot$ pot^{-1}]	Forms of lithium				
			F-1	F-2	F-3	F-4	F-5
1	0	0	0.260	0.140	0.212	0.709	6.36
2	10	0	0.515	0.406	0.238	0.822	9.71
3	20	0	0.931	0.671	0.242	1.224	6.95
4	10	26	0.472	0.393	0.212	0.446	8.14
5	20	26	0.976	0.664	0.226	0.415	7.72
6	10	56	0.440	0.444	0.299	0.362	7.66
7	20	56	0.972	0.780	0.340	0.462	7.76
8	10	78	0.507	0.437	0.310	0.468	8.08
9	20	78	0.810	0.735	0.340	0.349	7.82

Lithium doses of 10 and 20 mg Li per pot very distinctly affected the amount of lithium extracted using 2.5 % CH_3COOH as F-2 form. In this case a similar dependence occurred as in F-1 fraction.

The content of lithium bound to organic matter F-3, extracted with 0.1 mol $K_2P_4O_7 \cdot dm^{-3}$ ranged from 0.212 to 0.340 mg Li $\cdot$ kg^{-1}.The quantity of cation bound to organic matter extracted using 0.1 mol $K_2P_4O_7 \cdot dm^{-3}$ was visibly increasing on treatment with growing lithium doses. Assuming eg the amount of lithium bound to organic matter extracted on the control treatment with natural content of this element as 100, one may conclude that at increasing lithium doses the amount of extracted cation was greater by 12 and 14 %.

Application of organic matter dose of 52 and 78 g per pot on treatments with elevated lithium content caused an increase of the quantity of extracted cation bound to organic matter which was between 26 and 40 % bigger in relation to the control treatments with the same lithium level. This problem may be explained by the fact that in result of organic matter application sorption ability towards metals increases thus limiting their uptake by plants. The strength of metal bonding by organic matter is different for individual metals. Forming and durability of chelate bonds depend on the kind and molecular weight of humic acids [12]. Dziadowiec et al [13] declered that complexes of fulvic acids, due to smaller molecular weight and greater content of functional groups, are better soluble than humic acid complexes.

Lithium content in F-4 fraction extracted with Tamm reagent (0.1 mol $H_2C_2O_4 \cdot dm^{-3}$ + 0.175 mol $(NH_4)_2C_2O_4 \cdot dm^{-3}$) determined as the form adsorbed on the surface of Fe, Mn and Al oxides fluctuated from 0.349 to 1.224 mg Li $\cdot$ kg^{-1}. The amount of cation extracted using this reagent rose by 16 and 73 % with increasing doses of organic matter. Increasing doses of organic matter ie 26, 52 and 78 g per pot on treatments with growing lithium doses caused a decrease of the quantity of lithium extracted with Tamm reagent (0.1 mol $H_2C_2O_4 \cdot dm^{-3}$ + 0.175 mol $(NH_4)_2C_2O_4 \cdot dm^{-3}$) which was between 2 and 3.5 times smaller on these treatments (Table 5).

Conclusions

1. Contents of individual lithium forms obtained in result of metal sequencing extraction depended on natural content of this element in soil, lithium dose and the dose of applied compost (organic matter).

2. Increasing lithium doses applied as soluble salt (LiCl) in the amounts of 10 and 20 mg Li · pot^{-1} positively affected the amounts of cation extracted in individual forms in result of metal sequencing extraction.

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WPŁYW WŁAŚCIWOŚCI GLEBY A FITOPRZYSWAJALNOŚĆ LITU
Cz. 2. ZAWARTOŚĆ LITU W GLEBIE PO ZAKOŃCZONYM OKRESIE WEGETACJI

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Po zakończonym okresie wegetacji żyta pobrano próbki glebowe z każdej serii w celu prześledzenia zmian, jakie zaszły we właściwościach fizycznych i chemicznych. Wzrastające dawki materii organicznej oraz zastosowane dwie dawki litu powodowały zmiany właściwości fizycznych i chemicznych gleby. Zastosowane dawki litu oraz materii organicznej wpływały na wartość pH, wartość kwasowości hydrolitycznej, zawartość C-organicznego oraz na zawartość litu w glebie. W celu określenia zawartości litu oraz jego form w glebie wykorzystano metodę sekwencyjnej ekstrakcji metali, stosując roztwory o różnej sile ługowania: H_2O; 2,5 % CH_3COOH; 0,1 mol $K_2P_4O_7 \cdot dm^{-3}$; 0,1 mol $H_2C_2O_4 \cdot dm^{-3}$ + 0,175 mol $(NH_4)_2C_2O_4 \cdot dm^{-3}$. W wyniku sekwencyjnej ekstrakcji oznaczono formy litu od łatwo rozpuszczalnych, czyli dostępnych dla roślin, przez słabo związane z kompleksem sorpcyjnym, po trudno rozpuszczalne, nieuruchamiane, a więc niedostępne dla roślin. Zawartość litu w poszczególnych frakcjach była dość zróżnicowana. Czynnikami decydującymi o poziomie tego pierwiastka w poszczególnych formach w glebie były zastosowana dawka litu oraz wzrastające dawki materii organicznej, jednego z parametrów wpływających na kompleks sorpcyjny.

Zastosowane dawki litu w ilości 10 i 20 mg Li · $wazon^{-1}$ wpływały bardzo wyraźnie na ilość wyekstrahowanego litu przy użyciu H_2O – formy F-1, a zastosowane wzrastające dawki materii organicznej wpływały ograniczająco na ilość litu wyekstrahowanego przy użyciu H_2O. Zawartość litu związanego z materią organiczną F-3, ekstrahowanego 0,1 mol $K_2P_4O_7 \cdot dm^{-3}$, wahała się od 0,212 do 0,340 mg Li · kg^{-1}. Ilość kationu związanego z materią organiczną wyekstrahowanego 0,1 mol $K_2P_4O_7 \cdot dm^{-3}$ wyraźnie wzrastała w obiektach ze wzrastającymi dawkami litu.

Słowa kluczowe: formy litu w glebie, sekwencyjna ekstrakcja, właściwości gleby

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Wiesław SZULC[1], Beata RUTKOWSKA,
Wojciech STĘPIEŃ and Anna PODKOŃSKA

EVALUATION OF THE POSSIBILITY OF AGRICULTURAL USE OF SEWAGE SLUDGE COMPOST PRODUCED BY THE MUNICIPAL WASTEWATER PLANT IN THE CITY OF LOWICZ

OCENA MOŻLIWOŚCI ROLNICZEGO ZAGOSPODAROWANIA KOMPOSTU Z OSADU ŚCIEKOWEGO Z MIEJSKIEJ OCZYSZCZALNI ŚCIEKÓW W ŁOWICZU

Abstract: Evaluation of chemical properties of municipal sewage sludge compost was carried out in view of the possibility of agricultural use. The results obtained indicated neutral to acidic reaction of tested compost and the high content of nitrogen calcium and organic matter. At the same time, the levels of heavy metals did not exceed the norms for compost agricultural use. Therefore, this waste material can be used for plant fertilization in field cultivation. The maximum application rate of the analysed compost calculated taking into account the results obtained as well as the levels permitted in the Regulation of the Minister of Environment is limited by the content of zinc and it amounts to approximately 5 Mg of dry mass per ha annually, being equivalent to 11.5 Mg of fresh mass.

Keywords: compost, sewage sludge, fertilizer components, heavy metals, fertilization

Changes that have taken place in Polish agriculture have resulted in a reduction of farm animal stock, and then again the use of mineral fertilizers decreased. These have led to insufficient supply of nutrients and organic matter into soils. Such circumstances can lead to a decrease of indicator values of soil fertility and fecundity. Therefore, new sources of nutrient and organic matter supply into soils have been sought. One of these sources is sewage sludge from municipal wastewater. Currently, the production of sewage sludge in Poland amounts to 501.3 thousand tons of dry mass and only 16.0 7 % is used for agricultural purposes [1].

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[1] Department of Soil Environment Sciences, Warsaw University of Life Sciences (SGGW), ul. Nowoursynowska 159, 02–776 Warszawa, Poland, phone +48 22 593 2628, fax +48 22 593 2631, email: wieslaw_szulc@sggw.pl

Several studies have shown advantageous effects of sewage sludge application on physiochemical properties of soil as well as plant productivity and quality [2–6]. Municipal sewage sludge belong to the group of waste materials that should be a subject to the stabilisation process before designation to the use in agriculture. One of the methods of waste stabilisation is composting that allows to obtain valuable organic fertilizer, which at the same time is safe in terms of sanitary requirements [7–10].

Hence, this research was undertaken in order to evaluate changeability of the chemical content of sewage sludge compost as well as its environmental usefulness.

Material and methods

The trials were carried out on samples of compost obtained from sewage sludge collected at the Municipal Wastewater Treatment Plant in the city of Łowicz in the years 2005–2006. The compost was produced from municipal sewage sludge (70 %) and sawdust (30 %). Samples for compost analyses were collected 3 times a year. A representative sample was obtained by adding together and mixing thoroughly 10 individual samples collected in one go from different spots selected on the study prism. Test samples of approximately 1 kg were taken for further laboratory analyses.

The laboratory compost samples were dried with the use of a forced air drier at the temperature 105 ^{o}C and then ground. The following features were evaluated:

– reaction – with the use of potentiometric method,

– dry mass content – with the use of gravimetric method,

– organic matter content – after thermal decrepitation at 600 ^{o}C,

– the total nitrogen content – with the use of Kjeldahl method.

After wet mineralization in the mixture of nitric(V), chloric(VII) and sulphuric(VI) acids, there were determined:

– the total content of phosphorus – with the use of spectrophotometric method,

– the content of calcium, magnesium and heavy metals (lead, cadmium, nickel, zinc, copper and chromium) – with the use of the AAS method.

Chemical analyses were carried out according to the common methods of agricultural chemistry [11].

Results and discussion

The results of chemical analyses showed high contents of organic matter and nitrogen in examined compost (Table 1). Thus, a possibility of the use of this material for plant fertilization was shown. At the same time, the results of compost analyses on parasites and bacteria carried out by the District Centre of Sanitary and Epidemiologic Surveillance in the city of Skierniewice, did not show either pathological bacteria from the genus Salmonella or alive eggs of intestine parasite species, such as *Ascaris* sp., *Trichuris* sp. and *Toxocara* sp. This confirmed usefulness of analysed compost for natural utilization [12].

Table 1

Chemical properties of sewage sludge compost from the Municipal Wastewater Plant in the city of Lowicz

Timing of sample collection	pH	d.m. [%]	Organic matter [% d.m.]	Organic C	Total N	P	Ca	Mg	C:N
				$[g \cdot kg^{-1}$ d.m.]					
April 2005	5.8	46.7	66.2	384.0	26.4	17.1	32.5	5.3	14.5
August 2005	5.6	43.5	66.5	385.7	25.4	11.4	35.5	4.5	15.2
November 2005	5.9	34.3	72.1	418.2	23.1	10.9	29.6	4.8	18.1
April 2006	6.3	45.0	63.6	368.9	27.7	12.1	31.8	4.6	13.3
August 2006	6.5	47.3	58.4	338.7	26.6	13.6	36.8	5.3	12.7
November 2006	6.2	43.2	61.3	355.6	25.9	11.8	32.3	4.7	13.7
Average	—	43.3	64.7	375.2	25.9	12.8	33.1	4.9	14.6
$LSD_{0.05}$	not significant								

Investigated sewage sludge compost showed reaction from neutral to weak acidic (pH 5.6–6.5) as well as relatively high contents of calcium (33.08 g Ca $\cdot$ kg^{-1} d.m.) and magnesium (4.87 g Mg $\cdot$ kg^{-1} d.m.), which can be considered as advantageous because in Poland, a great quantity of acidic and very acidic soils has been observed [13].

The content of nitrogen and organic carbon as well as C:N ratio have an effect on the possibility of agricultural use of sewage sludge compost. The total N in investigated compost was from 23.1 to 27.7 g $\cdot$ kg^{-1} d.m., and the content of organic C ranged from 338.7 to 418.2 g $\cdot$ kg^{-1} d.m. (Table 1). These amounts are similar to those observed by other authors in pre-compost sewage sludge [5, 8]. The C:N ratio in investigated compost ranged from 12.7:1 do 18.1:1 (Table 1). Czekala [14] reported a high range of C:N ratio in sewage sludge examined in the region of Wielkopolska (from 5.3:1.0 to 21.9:1.0). C:N ratio of sewage sludge indicates a rate of its decomposition in soil. Therefore, this parameter should be taken into account during evaluation of sewage sludge for fertilizer purposes, in view of the fact that C:N ratio is crucial for the use of nitrogen by plants [15].

The total phosphorus in composted sewage sludge was on average 12.82 g $\cdot$ kg^{-1} d.m. When compared with observations by other authors, our end results indicated the total phosphorus in compost obtained from municipal sewage sludge were two fold lower than that reported by Izewska [5]. On the other hand, the content of phosphorus observed in this study was similar to the average content of this element in sewage sludge (raw and composted) tested in the region of Wielkopolska [14].

Sewage sludge and compost produced from it contain various amounts of heavy metals, such as lead, cadmium, nickel, zinc, copper and chromium, which can exclude this material as useful for agricultural purposes. The content of all heavy metals in sewage sludge compost analysed in this study was relatively low (Table 2) and did not exceed the levels permitted by the Regulation of the Minister of Environment on application of sewage sludge in agriculture [12].

Table 2

The content of heavy metals in sewage sludge from the Municipal Wastewater Plant in the city of Lowicz

Timing of sample collection	Pb	Cd	Zn	Cu	Cr	Ni
	$[\mathrm{mg \cdot kg^{-1}\ d.m.}]$					
April 2005	43.0	0.50	1064.0	201.0	63.8	16.1
August 2005	36.1	1.36	1014.0	312.0	57.0	16.5
November 2005	49.1	0.50	1046.0	283.0	62.3	13.8
April 2006	29.5	0.50	845.0	218.0	42.4	16.1
August 2006	33.4	1.26	1084.0	235.0	47.9	18.9
November 2006	41.8	0.50	968.0	310.0	46.6	14.4
Average	38.8	0.77	1003.5	259.8	53.3	16.0
Level permitted by law [12]	500	10	2500	800	500	100
$LSD_{0.05}$	not significant					

The maximum possible application rate for agricultural use of the analysed compost was calculated based on the obtained results on content of heavy metals and the levels granted in the Regulation of the Minister of Environment [12] (Table 3).

Table 3

The average content of heavy metals in sewage sludge compost and the maximum compost rate to use in agriculture

Heavy metal	Maximum annual rate of heavy metal* $[\mathrm{g \cdot ha^{-1}}]$	Heavy metal content in sewage sludge $[\mathrm{mg \cdot kg^{-1}\ d.m.}]$	Maximum annual rate of compost $[\mathrm{mg\ d.m. \cdot ha^{-1}}]$
Lead (Pb)	1000	38.82	25.8
Cadmium (Cd)	20	0.77	26.0
Nickel (Ni)	200	15.97	12.5
Zinc (Zn)	5000	1003.50	5.0
Copper (Cu)	1600	259.83	6.2
Chromium (Cr)	1000	53.33	18.8

* Regulation by the Minister of Environment [12].

The calculated results showed zinc as the element which is the most limiting factor for the possibility of agricultural use of tested sewage sludge compost. Based on the content of this element in analysed compost it was calculated that the maximum annual rate of this compost dry mass which can be applied in agriculture cannot exceed 5.0 $\mathrm{Mg \cdot ha^{-1}}$ per year (Table 3), which is equivalent to 11.5 Mg per $\mathrm{ha^{-1} \cdot year^{-1}}$ of fresh mass.

Conclusions

1. Compost produced from sewage sludge and sawdust by the Municipal Wastewater Plant in the city of Lowicz indicated neutral to acidic reaction and the high content of

nitrogen, phosphorus and calcium in organic matter. At the same time, the levels of heavy metals did not exceed the norms for agricultural use of such compost. Therefore, this waste material can be used for plant fertilization in field cultivation.

2. The use of analysed compost for soil fertilization can influence maintenance, yet improvement of organic matter content in soil which is harmony with the new soil directive elaborated by the EU.

3. The maximum application rate of analysed compost calculated taking into account the results obtained and the heavy metals levels granted in the Regulation of the Minister of Environment, is restricted by the content of zinc and it amounts to approximately 5 Mg of dry mass per ha annually, being equivalent to 11.5 Mg of fresh mass.

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OCENA MOŻLIWOŚCI ROLNICZEGO ZAGOSPODAROWANIA KOMPOSTU Z OSADU ŚCIEKOWEGO Z MIEJSKIEJ OCZYSZCZALNI ŚCIEKÓW W ŁOWICZU

Katedra Nauk o Środowisku Glebowym
Szkoła Główna Gospodarstwa Wiejskiego w Warszawie

Abstrakt: Dokonano oceny składu chemicznego pod kątem możliwości rolniczego wykorzystania kompostu z komunalnego osadu ściekowego.

Na podstawie przeprowadzonych badań stwierdzono, że badany kompost charakteryzuje się odczynem słabo kwaśnym do obojętnego oraz dużą zawartością substancji organicznej, azotu i wapnia. Jednocześnie zawartość metali ciężkich nie przekracza norm umożliwiających rolnicze wykorzystanie tego kompostu. W związku z tym odpad ten może być wykorzystywany do nawożenia roślin w uprawie polowej. Maksymalna dopuszczalna dawka tego kompostu, obliczona zgodnie z ilością podaną w Rozporządzeniu Ministra Środowiska i zawartością metali ciężkich w badanym kompoście, jest limitowana przez cynk i wynosi około 5,0 Mg suchej masy na ha rocznie, co odpowiada dawce 11,5 Mg świeżej masy.

Słowa kluczowe: kompost, osad ściekowy, składniki nawozowe, metale ciężkie, nawożenie

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Andrzej WALKOWIAK[1]

EFFECTIVENESS OF DAIRY WASTE TREATMENT IN AN INTEGRATED BIOLOGICAL REACTOR

EFEKTYWNOŚĆ OCZYSZCZANIA ŚCIEKÓW MLECZARSKICH W ZINTEGROWANYM BIOREAKTORZE

Abstract: Processes of anaerobic decomposition of sewage are used, among others, for sewage treatment in the agrarian-food sector, including dairy waste treatment. The research concerned dairy waste treatment in anaerobic conditions using original packing. The aim of the research was to determine the influence of the concentration changes of organic sewage in the sewage flowing into the anaerobic reactor on the treated waste COD value. The directions of biochemical changes being one of the factors determining the level of organic sewage in the treated sewage was evaluated on the basis of the reaction of waste, expressed as a pH. During a three-month period of research the intensity of raw sewage was gradually increased, observing lower and lower COD value of the treated sewage. At the end of the IV stage of the research the degree of reduction of organic sewage in treated sewage, in relation to raw sewage, was 81 %.

Keywords: anaerobic reactor, dairy waste, packing (molders), COD, treatment effectiveness

One of the main trends in waste management is, at present, waste recycling which means reusing worn out materials again and using them as materials for producing new, high-quality products. In this research the efficiency of treating model dairy waste in anaerobic conditions was tested in a half-technical scale. The packing of the reactor was made from waste materials. The development of an agrarian-food sector makes on-site sewage treatment facilities, which in the past treated sewage sufficiently, unable to meet the requirements today.

The fact that Poland joined the EU is connected with toughening the regulations of environmental protection, including rational water-sewage management. The European directive concerning integrated prevention and sewage limit, imposes an obligation on production plants to regulate immediately water-sewage management and to be in possession of so-called integrated permits. That is why the necessity to adjust Polish regulations to EU norms requires building new on-site sewage facilities or modern-

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[1] Department of Environment Protection Engineering, The University of Warmia and Mazury in Olsztyn, ul. I. Prawocheńskiego 1, 10–957 Olsztyn, Poland, email: a.walkowiak@uwm.edu.pl

ization already existing ones [1]. The second solution is chosen by many producers, enhancing the effectiveness of waste treatment.

In the dairy industry it is a very important issue because this industry uses a lot of water. The use of water in this industry is one of the biggest in all the branches of food industry. Water demand indicators for technological reasons (production processes, power industry, devices cleaning) are at the level of 3–20 $m^3 \cdot m^{-3}$ of processed milk [2]. In this context proper water-sewage management seems to be very important.

Apart from a high degree of organic components liquidation, there are a few other advantages of sewage decomposition in anaerobic conditions such as: production of sewage gas, low energy need, low increase of microorganism biomass and possibility to implement anaerobic reactors after a long exploitation break [1].

The aim of the research was to determine the influence of organic sewage concentration in the sewage flowing to the anaerobic reactor on COD value of treated sewage.

Materials and methods

The reactor, exploited during the research, is in the shape of two cylindrical pipes concentrically positioned. The diameter of the outer pipe was 88 mm, and of the inner one –188 mm (Fig. 1).

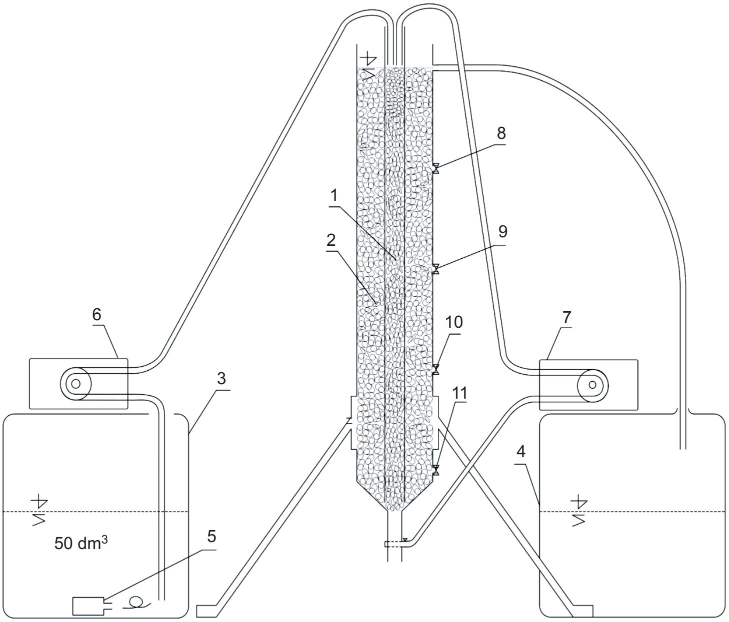

Fig. 1. Bioreactor (construction of research stand) (own study under the direction of prof. DrSc. M. Krzemieniewski in the Department of Environmental Protection Engineering: 1, 2 – reaction chambers, 3 – container of raw sewage, 4 – treated sewage tank, 5 – draught pump, 6 – pump dispensing sewage, 7 – recirculation pump, 8, 9 – sewage discharge stub pipes, 10, 11 – sewage and deposit discharge stub pipes

Space inside each of the pipes formed a reaction chamber, in which bioactive packing (moulders) have been placed. This plenum was made on the base of waste plastics with admixture of chemical substances. The moulders are in the shape of a cylinder with a hollow, non-concentric hole. An average height of the moulder is 24.4 mm, and its external diameter is 88 mm.

In order to standardize the quality composition of sewage flowing into the reactor, a draught pump was placed in the raw sewage container. From this container sewage was led to the inner pipe of the reactor. Gravitational sewage flowed downwards, next they emerged in the lower part of the reactor and flowed into the outer pipe, in which ascending floating of sewage took place. From the outer pipe the sewage floated through the discharge of treated sewage inflow placed in the upper part of the device. The bottom, conical part of the reactor was finished with a sewage and deposit discharge.

The bioreactor, which is 2.75 m high, was equipped with discharge stub pipes enabling taking waste for analysis. These discharge stub pipes are placed on the four heights of the reaction chamber: at 0.2 m, 0.8 m, 1.4 m and 2 m. About 5600 moulders were placed in the reactor, total surface of which is about 134 m^2.

25 dm^3 of digested deposit from Municipal Sewage Treatment Plant in Olsztyn, and simulated dairy waste prepared from 40 g of powdered milk solved in 45 dm^3 of water from water supply system were put into the reactor (COD = 580 mg $O_2 \cdot dm^{-3}$). From this moment a biological process of adaptation of bacterial microflora to the content of sewage began. This process required gradual adaptation of microorganisms to sewage environment and gradual growing of anaerobic bacterial microflora on the surface and inside constructed packing. With time of prolonging the adaptation of bacterial flora penetration and immobilization of bacterial flora inside the packing structure took place. During this process, every day, simulated dairy waste was put into the reactor, which was the nutrient medium for bacteria and the sewage and sludge reaction of sewage and sludge in the reactor were controlled currently.

In order to create a better immobilization of microorganisms on the surface of the packing, after 27 days from the start of the reactor exploitation, sludge and sewage which were in the reactor were flashed. Next, fresh and digested anaerobic sludge and simulated dairy sewage were placed.

The effectiveness of dairy sewage treatment in anaerobic conditions was analyzed at the four research stages, in four different concentrations of organic substances in simulated dairy waste flowing into the reactor:

– I research stage – 20 g of permeate in 50 dm^3 of waterworks water (COD = 366 mg $O_2 \cdot dm^{-3}$); this stage lasted 6 days,

– II research stage – 20 g of permeate + 20 g of powdered milk (skimmed) in 50 dm^3 of waterworks water (COD = 525 mg $O_2 \cdot dm^{-3}$); this stage lasted 7 days,

– III research stage – 50 g of permeate + 20 g of powdered milk (full-cream) in 50 dm^3 of waterworks water (COD = 1605 mg $O_2 \cdot dm^{-3}$); this stage lasted 21 days,

– IV research stage – 50 g of permeate + 40 g of powdered milk (full-cream) in 50 dm^3 of waterworks water (COD = 1719 mg $O_2 \cdot dm^{-3}$); this stage lasted 5 days.

Based on pH changes in the sewage and deposit in the reactor during its exploitation and pH changes of treated sewage, COD value of sewage flowing into the device was increased or kept at the constant level.

In winter months, in the outer pipe under the surface of sewage, an aquarium heater was placed, which kept the temperature of sewage in the reactor between 17.9 to 25 °C.

Results

The reaction of raw sewage and treated sewage at different research stages, expressed as pH was as follows:

- I research stage (COD of raw sewage was 366 mg $O_2 \cdot dm^{-3}$),
  a) raw sewage from 6.1 to 6.2,
  b) treated sewage from 6.1 to 6.2,
- II research stage (COD of raw sewage was 525 mg $O_2 \cdot dm^{-3}$),
  a) raw sewage from 5.5 to 6.1,
  b) treated sewage from 5.9 to 6.6,
- III research stage (COD of raw sewage was mg $O_2 \cdot dm^{-3}$),
  a) raw sewage from 5.6 to 7.7,
  b) treated sewage from 6.5 to 7.5,
- IV research stage (COD of raw sewage was 1719 mg $O_2 \cdot dm^{-3}$),
  a) raw sewage from 6.6 to 7.3,
  b) treated sewage from 6.9 to 7.7.

A graphic image of raw waste reaction (flowing into the reactor) and treated waste (outflow) was presented in Fig. 2.

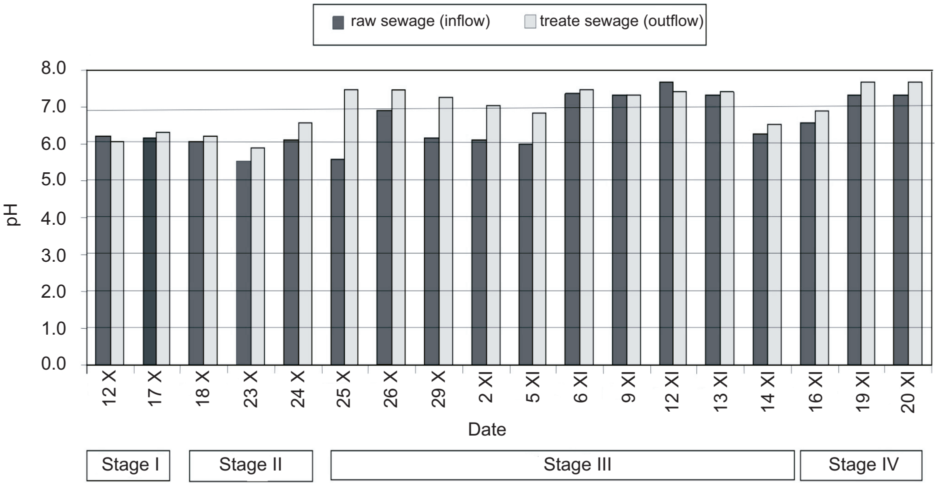

Fig. 2. Course of pH reactions in raw sewage for the inflow and treated sewage on the outflow (own research)

The second analyzed parameter was the degree of reduction of organic pollution, in the treated sewage in the ratio to raw sewage. At different research stages the following was observed:

– I research stage – organic waste concentration in the sewage on the outflow was higher than in the waste flowing into the reactor,

– II research stage – decrease of COD value in treated sewage (from 34 % to 46 %) in ratio to raw sewage,

– III research stage – from 46 % of the increase of waste concentration in the sewage flowing off the reactor to 75 % reduction,

– IV research stage – decrease of COD value in treated sewage (from 62 % to 81 %) in ratio to raw sewage.

The completion of a given research period and passing to the next one, took place only then when pH of treated sewage stayed at a similar level for a few consecutive days or was beginning to increase.

The increase of the concentration of pollution in the raw waste caused the increase of the reduction degree of COD from sewage. At the research stage, when the highest COD value of inflowing waste was used (stage IV – COD = 1719 mg $O_2 \cdot dm^{-3}$), the highest reduction of concentration of pollution – 81 % (Fig. 3) was observed.

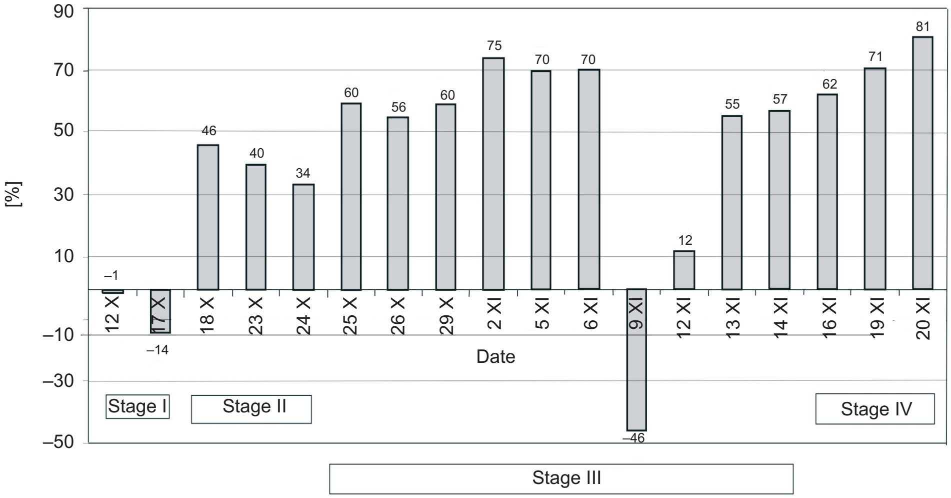

Fig. 3. Degree of COD reduction [%] (own research)

At the first stage of the experiment and after a one-month period from the start of the research the increase of the concentration of organic sewage in the treated sewage was observed in the ratio to raw sewage. It was caused by wiping of sludge introduced to the reactor, which had not been as a result of adsorption, absorption and immobilization of bacterial flora bonded on the surface and inside the plenum. With the passage of the research time at each stage (constant concentration of organic sewage in sewage flowing into the reactor) the increase of the effectiveness of treated sewage, expressed as a lower concentration of treatment in treated sewage was noticed. Possible exceptions to the rule were caused by the changes of sewage temperature (Fig. 4), and connected with it pH changes (Fig. 2).

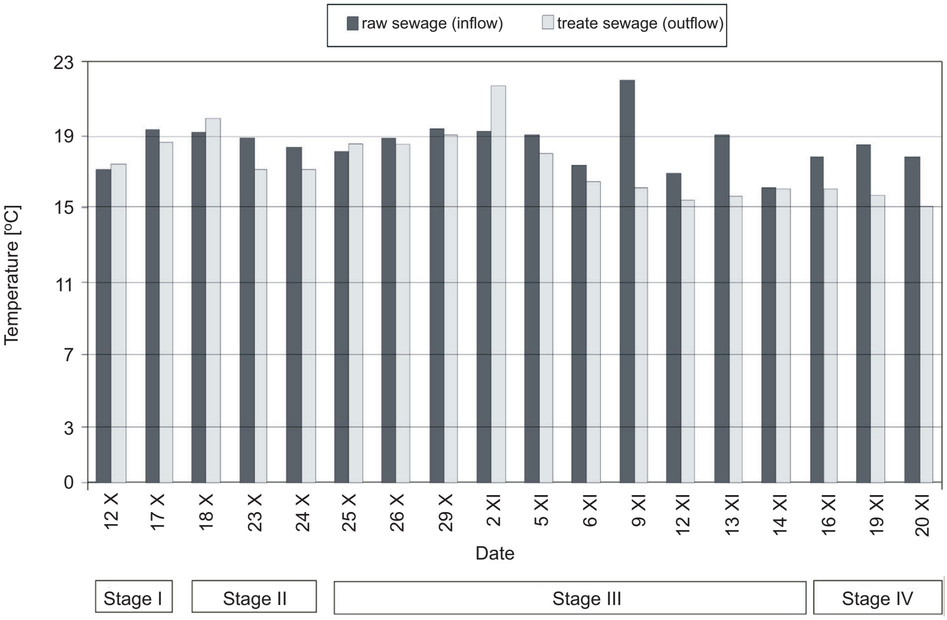

Fig. 4. Temperature [^{o}C] changes course in raw sewage on the outflow and treated sewage on the inflow (own research)

Due to the fact that the research published in this paper has application character, for the whole research period it has been tried to keep the temperature of the surroundings, close to temperatures existing in natural conditions in on site sewage facilities of dairy plants. Outside air temperature shaped the raw sewage temperature and further also the temperature of the treated sewage.

Results and discussion

One of the factors determining the intensity of waste treatment is the intensity of biochemical processes taking place in the reactor. It was evaluated based on the changes of the values of the reaction pH of treated sewage and sewage located in the reactor [3].

At all research stages, at the beginning the decrease of the sewage pH was observed, and next its value increased. The observed reaction was the result of the fact that dairy waste has a tendency to putrefy because of the accumulation of butyric acid created by fermentation of lactose and taking place at the same time, butyric fermentation [4].

The reaction influences directly the effectiveness of waste treatment because the majority of microorganisms responsible for biological decomposition of organic substances prefer pH within the range from 6.0 to 8.0 [5, 6]. That is why, at given research stages pH was tried to be kept at this level. The completion of a given research stage and start of a new one was connected with the increase of COD value of sewage flowing into the reactor and took place when pH was higher than 6.0 or stayed at the similar level for the few consecutive days.

The degree of reduction was within the range from 12 to 81 % reaching values over 70 % in the middle of III and at the end of IV research stages.

During the first stage a bigger concentration of organic pollution in the sewage from the reactor was noticed in the ratio to the sewage flowing into the reactor. It was caused by scouring of digested sludge from the reactor before the research period. During this period of adaptation of sludge (27th September – 17th October) penetration and immobilization of bacterial flora on the surface and inside the plenum structure took place. A similar situation was observed at the beginning of the second half of the third stage, when to improve immobilization of microorganisms, digested sludge and sewage in the reactor were disposed of through the discharge stub pipe, and the bioreactor was filled with fresh digested sludge again.

Conclusions

Microorganisms existing as biological membrane on the surface of a reactor plenum adopt very quickly to the increasing concentration of the organic substances in the sewage flowing off the reactor.

1. In this research it has been confirmed that treatment of dairy waste in anaerobic conditions provided positive results. At the end of the three-month research period the reduction of 81 % of the content of organic pollution in treated waste was obtained.
2. The degree of reduction of organic pollution is dependent on the concentration of pollution in the sewage flowing into the reactor. During gradual increasing of the concentration of organic sewage in raw sewage, bigger and bigger reduction of COD value in treated sewage was observed.
3. The longer the period of the given research stage was, the higher the increase of the reduction degree was observed.
4. At the beginning of each stage pH value decrease was observed which was the effect of sewage putrescibility.

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EFEKTYWNOŚĆ OCZYSZCZANIA ŚCIEKÓW MLECZARSKICH W ZINTEGROWANYM BIOREAKTORZE

Katedra Inżynierii Ochrony Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Procesy beztlenowego rozkładu zanieczyszczeń są wykorzystywane m.in. do oczyszczania ścieków branży rolno-spożywczej, w tym ścieków mleczarskich. Badania dotyczyły oczyszczania ścieków mleczarskich w warunkach beztlenowych z wykorzystaniem nowatorskiego wypełnienia. Celem badań było określenie wpływu zmian stężenia zanieczyszczeń organicznych w ściekach dopływających do bioreaktora beztlenowego na wartość ChZT ścieków oczyszczonych. Kierunki przemian biochemicznych, będące jednym z czynników determinujących poziom zanieczyszczeń organicznych w ściekach oczyszczonych oceniano na podstawie odczynu ścieków, wyrażonego jako pH.

W trakcie trwających trzy miesiące badań stopniowo zwiększano stężenie zanieczyszczeń organicznych ścieków surowych, obserwując coraz mniejsze ChZT ścieków oczyszczonych. Na końcu IV etapu badań stopień redukcji zanieczyszczeń organicznych w ściekach oczyszczonych, w stosunku do ścieków surowych, wyniósł 81 %.

Słowa kluczowe: bioreaktor beztlenowy, ścieki mleczarskie, wypełnienie, ChZT, efektywność oczyszczania

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Józefa WIATER[1] and Adam ŁUKOWSKI[1]

MOBILITY OF LEAD IN CONDITIONS OF ACID SOILS OF PODLASIE REGION

MOBILNOŚĆ OŁOWIU W WARUNKACH KWAŚNYCH GLEB PODLASIA

Abstract: The researches were conducted in three districts of Podlasie Region. The research covered the determination of total content of lead and its two fractions: I (lead in soil solution, exchangeable) and II (lead bound with oxides and hydroxides of Fe and Mn). There was determined also pH of soils, the content of organic carbon in them, base exchange capacity and hydrolytic acidity.

It was found that the content of carbon in analyzed soils was low and typical for slightly contaminated soils. The content of both mobile fractions of lead was also low, but the percentage in total content was high and ranged between 12.8 and 36 %.

Keywords: acid soils, lead, mobility, fractions

The occurrence of lead in soils is in a direct relation with their mineralogical and glanurometrical composition, the origin of parent rock of soils, traffic and industrial emission and the use of industrial waste and municipal sewage sludge in liming [1–4].

Lead in soil environment is less mobile than cadmium and zinc, however it moves easily into food chain in a condition of soil contaminations. Acid reaction of soils, low content of humus and low sorptive capacity is in favour of excessive lead uptake by plants [5]. The conditions which limit the uptake of this element by plants is liming, organic and phosphorus fertilization [4, 6]. Dziadek and Waclawek [7] claim that phosphorus introduced into the soil contaminated by lead decreases slightly the amount of its easily soluble forms and forms bound with carbonates and oxides, while it causes the increase of organic fractions content and most of all share of fractions strongly bound with residual remains. After intake of lead into soils in the form of different inorganic compounds, it surrenders to absorption on organic and mineral colloids and it creates stable and insoluble in water chelation combinations with organic compounds. Sparingly soluble hydroxides $PbOH^+$, phosphates and carbonates of lead $Pb(CO_3)_2$

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[1] Department of Technology in Engineering and Environmental Protection, Bialystok University of Technology, ul. Wiejska 45a, 15–351 Białystok, Poland, phone 85 746 96 44, email: kbt@pb.bialystok.pl

precipitate in soils with slightly acid, neutral and alkaline reaction. A part of lead in acid soils occurs in forms of Pb^{2+} and $PbHCO_3^+$ which are easily available for plants. Soils which are not under direct influence of contaminations do not show the tendency of lead accumulation. Lead content in geochemical background of soils in Poland amounts 20 $mg \cdot kg^{-1}$. In soils formed from sands it is even lower and amounts to 16 $mg \cdot kg^{-1}$ on average [4].

As far as the content of heavy metals is concerned, soils in Poland are assessed on the basis of their total content, however the main danger for plants is their content in easily available forms [8]. That is why the aim of presented researches was the assessment of chosen soils of Podlasie region, taking into account the content of mobile forms of lead, which is considered as one of the most dangerous element for people and animals.

Material and methods

The samples for researches were taken from arable layer of soils in three districts of Podlasie province (105 samples) after plants crop in 2007. In soil samples there was determined the total content of lead after mineralisation in concentrated nitric(V) acid and two fractions modified by BCR method (Community Bureau of Reference, nowadays Standards Measurement and Testing Programme) [9]. It concerns fractions of metals: exchangeable, soluble in water and light acid bound with carbonates (1 stage), iron and manganese hydroxides (2 stage) and organic matter (3 stage). On the first stage of sequential analysis acetic acid is used (0.11 $mol \cdot dm^{-3}$), on the second one – hydroxylamine hydrochloride (0.5 $mol \cdot dm^{-3}$), but on the third one – hydrogen peroxide and ammonium acetate (1 $mol \cdot dm^{-3}$, pH = 2).

In the conducted researches there were determined two most mobile fractions: soluble fraction in 0.11 $mol \cdot dm^{-3}$ of acetic acid and reducible fraction (iron and manganese oxides), which was extracted by 0.5 $mol \cdot dm^{-3}$ of hydroxylamine hydrochloride solution. The fraction bound with organic matter was passed because of minimal content of carbon in analyzed soils. The determination of lead was done by atomic absorption spectrometry (Flame Atomic Absorption Spectrometry). There was counted the share of individual fractions and their sum in total content of lead. Moreover, there was determined agronomic category of soils, pH of soils in 1 $mol \cdot dm^{-3}$ of KCl solution, organic carbon measured by carbon analyzer – Total Organic Carbon 1200 as well as hydrolytic acidity and base exchange capacity by Kappen method.

Results and discussion

Most of analyzed soils from three districts of Podlasie region (94 samples) were classified to very acid (pH < 4.5) and acid (pH 4.5–5.5) soils. Only 8 soils from Kolno district were slightly acid (pH 5.5–6.5) and 3 were neutral (pH > 6.5) (Table 1).

Table 1

Physicochemical properties of soils

Range of pH and number of soils	Parameter	Organic carbon	Hydrolytic acidity	Base exchange capacity	Sorptive capacity
		[g C · kg^{-1}]	[mmol H^{+} · kg^{-1}]	[mmol(+) · kg^{-1}]	
Jasionowka					
< 4.5 n = 21	range	0.5–4.9	27–78	16–80	69–158
	$\bar{x}$	2	61.4	42.5	104
4.5–5.5 n = 11	range	0.8–3.1	33–69	32–144	74–180
	$\bar{x}$	1.8	45.3	60.7	106
Korycin					
< 4.5 n = 23	range	0.7–4.3	39–72	20–116	62–164
	$\bar{x}$	2.3	45.5	41.9	87.4
4.5–5.5 n = 10	range	0.6–4.3	24–60	32–88	59–112
	$\bar{x}$	2.1	36.6	52	88.6
Kolno					
< 4.5 n = 17	range	0.9–5.3	21–111	4–172	59–193
	$\bar{x}$	2.5	60.3	38.8	99.2
4.5–5.5 n = 12	range	0.7–4.9	21–69	28–152	67–201
	$\bar{x}$	2.7	51.5	74.3	125.8
5.5–6.5 n = 8	range	1.1–4.3	27–51	16–100	59–145
	$\bar{x}$	2.9	33	5.3	95
> 6.5 n = 3	range	1.7–5.5	15–21	132–260	153–281
	$\bar{x}$	3.6	19	174.7	205.7

According to agronomical category over 90 % of soils was very light and light and the rest was medium-heavy. The content of organic carbon in most soils was low and amounted to 2 g C · kg^{-1}. Slightly more carbon was determined in soils of Kolno district and its content ranged from 0.7 to 5.6 g · kg^{-1}. Most of soils demands liming application which is proved by pH in 1 mol KCl and the level of hydrolytic acidity, which fluctuated from 27 to 78 mmol H^{+} · kg^{-1} in very acid and acid soils from Jasionowka district. Similar values of this parameter were found in soils from other districts. Smaller acidity was determined in soils of neutral reaction from Kolno district. Sorptive capacity of analyzed soils was low and only in some cases it exceeded 200 mmol · kg^{-1}.

The analyzed soils had very low content of total lead (Table 2) which amounted to 2.8 mg · kg^{-1} on average in soils from Kolno district, 3.6 mg · kg^{-1} in soils from Korycin district and in soils from Jasionowka district lead content was higher and equaled 5.7 mg · kg^{-1}. These values indicate that there is no contamination by lead in analyzed soils.

Table 2

The content of total lead and its mobile forms [mg · kg^{-1}] as well as share of mobile forms in total Pb amount [%]

Range of pH and number of soils	Parameter	Total lead	Fraction I (soluble)		Fraction II (reducible)		Σ I and II fractions	
			content	share	content	share	content	share
Jasionowka								
< 4.5 n = 21	range	0.5–12.5	0.0–0.3	0.3–58.3	0.1–0.5	0.2–58.0	0.2–0.7	2.1–106.0
	$\bar{x}$	6.3	0.2	6.0	0.3	7.9	0.4	12.8
4.5–5.5 n = 11	range	1.0–11.5	0.0–0.3	0.5–29.7	0.1–0.3	1.6–28.3	0.2–0.6	2.1–58.0
	$\bar{x}$	5.5	0.2	6.2	0.2	6.6	0.4	12.8
Korycin								
< 4.5 n = 23	range	1–6.5	0.3–0.5	5.9–41.6	0.2–0.5	4.4–48.0	0.6–0.9	12.3–89.5
	$\bar{x}$	3.6	0.4	15.2	0.3	13.1	0.7	28.3
4.5–5.0 n = 10	range	1.0–5.0	0.3–0.5	8.2–36.3	0.3–0.4	6.2–26.2	0.6–0.8	14.5–62.5
	$\bar{x}$	3.6	0.4	13.7	0.3	11.4	0.7	25.2
Kolno								
< 4.5 n = 17	range	1.0–7.5	0.0–2.5	0.0–50.2	0.2–0.7	3.4–38.9	0.5–3.0	10.5–89
	$\bar{x}$	3.5	0.5	18.5	0.4	15.3	0.9	33.7
4.6–5.5 n = 12	range	1–5.0	0.0–1.2	0.0–47.4	0.3–0.7	5.83–49.7	0.5–1.6	15.6–62.6
	$\bar{x}$	2.8	0.5	18.2	0.4	17.8	0.9	36.0
5.5–6.5 n = 8	range	0.5–2.5	0.5–0.6	10.3–96.7	0.05–0.4	5.2–21.4	0.5–1.0	15.5–49.7
	$\bar{x}$	3.0	0.5	29.8	0.3	11.2	0.8	25.7
> 6.5 n = 3	range	2.5–2.5	0.0–5.2	0.0–20.6	0.3–0.3	11.6–13.7	0.3–0.8	12.4–32.9
	$\bar{x}$	2.5	0.3	13.3	0.3	12.5	0.6	25.4

The results of researches conducted by Terelak [4] in soils on arable land in Poland show that the average content of this element was 13.6 mg · kg^{-1}, with the range of 7.4 to 25 mg · kg^{-1}, however arable land of Podlasie province was characterised by the lowest content of lead throughout the country. While conducting the researches of soils on arable land of eastern Poland, Raczuk and Tkaczuk [10] found higher content of Pb, which ranged from 9.4 to 14.2 mg Pb · kg^{-1}. According to Bozko and Puchty [11] arable land of Poland is classified to uncontaminated by lead, which proves the results of Terelak et al [4]. The low content of this element in most soils of the country is caused by high content of light soils (60 %) which contain 20 % of floatable fractions. According to Kabata-Pendias and Pendias [3], the content of lead in soils formed from sands is generally lower in comparison with the content of this metal in soils made of more solid deposits. Similar relation found Czekala et al [12] while analysing arable soils of former Poznan province. The average content of lead in very light soils amounted to 15.8 mg · kg^{-1}, in light – 16.0 mg · kg^{-1}, in medium heavy – 18.3 mg · kg^{-1}

while in heavy ones – 18.8 mg · kg^{-1}. The influence of reaction on the content of this element in analyzed soil deposits was very weak.

The content of lead in first and second fraction in analyzed soils was at the similar level (Table 2). However, their share in total content of lead was slightly higher in case of the first fraction than in the second one in soils from Kolno district. The percentage of sum of two fractions containing easily soluble combinations of lead decreased in these soils together with the increase of pH and it reached: 33.7 % in very acid soils, 36.0 % in acid soils, 25.7 % and 25.4 % in lightly acid and neutral ones. In soils from the rest of districts, the content of lead in both fractions was similar but their share in total lead was different. In very acid and acid soils from Jasionówka first lead fraction constituted about 6 %, in acid soils from Korycin amounted 13.7 % and in very acid ones it equaled 15.2 %. Similar relations were found in soils from these districts in case of second fraction of lead. Karczewska [13], Keizer and Bruggenwert [14] prove strong influence of iron oxides in lead fixation especially in acid soils. The percentage of both fractions in total content of Pb indicates its highest mobility in soils from Kolno district, a little less in those from Korycin and the least from Jasionowka. Variation coefficient for individual fraction of lead was high and reached respectively for I and II fraction: 66.3 % and 34.7 % in Kolno district, 34.7 % and 52.0 % in Jasionowka, and 11.8 % and 16.0 % in Korycin district. There was not observed essential relation between active forms of lead, agronomical category and soil reaction. While conducting soil researches of arable land of Podlasie province Skorbilowicz et al [15] registered higher contents of active forms of lead that the ones presented in this paper, which fluctuated between 2.9 and 14.5 mg · kg^{-1} with the share in total lead content ranging from 7.3 to 36.1 %. The contents of exchangeable form of Pb in arable soils of Malopolska province ranged from 0.63 to 37.5 mg · kg^{-1}, with the average of 8.44 mg · kg^{-1} [16]. The mobility of lead was influenced mainly by acid reaction of soils and low content of organic matter. Terelak et al [4] found that excessive uptake of lead and other heavy metals is caused by acid reaction of soils, low content of humus and low sorptive capacity. Lead is very strongly bound by organic matter in soils with pH > 4.5. It is proved by the results obtained for lightly acid and neutral soils from Kolno district, where the percentage of mobile forms of lead was lower than in soils with higher pH values. Filipek-Mazur and Gondek [17] in their researches claimed that lead was bound mainly with organic matter within the range of 39–43 % in total content. The amount of lead bound with manganese and iron oxides reached 20 % of total content that is much more than in analyzed soils. Analyzed soils contained very little organic matter that is why a large part of lead stays in residual fraction. The researches of speciation of heavy metals in poor soil conducted by Pakula and Kalembasa [18] prove that the share of lead in this fraction fluctuated between 36.8 and 51.6 %.

Conclusions

1. The analyzed soils were characterised by acid and very acid reaction, high hydrolytic acidity and low content of organic carbon.
2. The content of total lead in soils was low and classified to natural values.

3. The higher share of mobile fractions of lead in total its content (about 30 %) was found in very acid and acid soils from Kolno and Korycin district, and distinctly lower (about 13 %) in soils from Jasionowka district.

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MOBILNOŚĆ OŁOWIU W WARUNKACH KWAŚNYCH GLEB PODLASIA

Katedra Technologii w Inżynierii i Ochronie Środowiska
Politechnika Białostocka

Abstrakt: Przeprowadzono badania gleb w trzech gminach Podlasia. W glebach oznaczono ogólną zawartość ołowiu i dwie jego frakcje I (ołów w roztworze glebowym oraz wymienny) i II (ołów związany z tlenkami oraz wodorotlenkami Fe i Mn). Oznaczono także pH gleb, zawartość w nich węgla organicznego, sumę zasad wymiennych i kwasowość hydrolityczną.

Stwierdzono, że zawartość ołowiu w badanych glebach była bardzo mała, typowa dla gleb lekkich niezanieczyszczonych. Również zawartość obu mobilnych frakcji ołowiu była mała, ale ich udział w zawartości ogólnej był znaczny i wahał się od 12,8 do 36 %.

Słowa kluczowe: gleby kwaśne, ołów, mobilność, frakcje

Varia

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Prof. dr hab. Maria Wacławek
Przewodnicząca Komitetu Organizacyjnego
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Maria.Waclawek@o2.pl
lub mrajfur@o2.pl
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