SOCIETY OF ECOLOGICAL CHEMISTRY AND ENGINEERING

ECOLOGICAL CHEMISTRY AND ENGINEERING A

CHEMIA I INŻYNIERIA EKOLOGICZNA A

Vol. 19 No. 1–2

OPOLE 2012

EDITORIAL COMMITTEE
Witold Wacławek (Society of Ecological Chemistry and Engineering, PL) – Editor-in-Chief
Marina V. Frontasyeva (Joint Institute for Nuclear Research, Dubna, RU) – heavy metals and radionuclides
Vasil Simeonov (University of Sofia, BG) – monitoring
Maria Wacławek (Opole University, PL) – alternative energy sources
Barbara Wiśniowska-Kielian (University of Agriculture, Kraków, PL) – agricultural chemistry

PROGRAMMING BOARD
*Witold Wacławe*k (Society of Ecological Chemistry and Engineering, PL) – Chairman
Jerzy Bartnicki (Meteorological Institute – DNMI, Oslo-Blindern, NO)
Mykhaylo Bratychak (National University of Technology, Lviv, UA)
Bogusław Buszewski (Nicolaus Copernicus University, Toruń, PL)
Eugenija Kupcinskiene (University of Agriculture, Kaunas, LT)
Bernd Markert (International Graduate School [IHI], Zittau, DE)
Nelson Marmiroli (University, Parma, IT)
Jacek Namieśnik (University of Technology, Gdańsk, PL)
Lucjan Pawłowski (University of Technology, Lublin, PL)
Krzysztof J. Rudziński (Institute of Physical Chemistry PAS, Warszawa, PL)
Manfred Sager (Agency for Health and Food Safety, Vienna, AT)
Mark R.D. Seaward (University of Bradford, UK)
Pavlina Simeonova (Bulgarian Academy of Sciences, Sofia, BG)
Petr Škarpa (Mendel University of Agriculture and Forestry, Brno, CZ)
Piotr Tomasik (University of Agriculture, Kraków, PL)
Roman Zarzycki (University of Technology, Łódź, PL)
Małgorzata Rajfur (Opole University, PL) – Secretary

STATISTICAL EDITORS
Władysław Kamiński (Technical University, Łódź, PL)
Zbigniew Ziembik (Opole University, Opole, PL)

LANGUAGE EDITOR
Ian Barnes (University of Wuppertal, Wuppertal, DE)

EDITORIAL OFFICE
Opole University
ul. kard. B. Kominka 6, 45–032 OPOLE, PL
phone: +48 77 455 91 49
email: waclawek@uni.opole.pl

SECRETARY
Małgorzata Rajfur
phone: +48 77 401 60 42
email: mrajfur@o2.pl

Copyright © by
Society of Ecological Chemistry and Engineering, Opole

Ecological Chemistry and Engineering A / Chemia i Inżynieria Ekologiczna A
is partly financed by Ministry of Science and Higher Education, Warszawa

ISSN 1898–6188

CONTENTS

Jolanta JONIEC and Jadwiga FURCZAK – Numbers and Activity of Selected Microbial Groups Involved in Carbon Transformations in Podzolic Soil Amended with Sewage Sludge 7

Bogdan SZOSTAK – Chemical Pollution of Soil and Water on Pig-Breeding Farms . . . 25

Jean B. DIATTA – Application of Geochemical Indices for Assessing Lead and Cadmium Contamination in Recreational Parks of the City Poznan 35

Ireneusz GRZYWNOWICZ – Potential Environmental Management of Waste Products from Exploratory Drilling Activities 45

Anna IŻEWSKA, Justyna CHUDECKA, Tomasz TOMASZEWICZ and Mariola WRÓBEL – Content of Macro- and Microelements in Roadsides' Top Layer of Forest Areas and Characteristics of Plant Species Settled 53

Monika JAKUBUS, Zbigniew KACZMAREK and Agnieszka WOLNA-MARUWKA – Changes of some Selected Soil Properties Incubated with the Addition of Agar, Starch and Effective Microorganisms 61

Andrzej PLAK, Piotr BARTMIŃSKI and Ryszard DĘBICKI – Some Regularities in Accumulation and Migration of Heavy Metals (Cd, Cu, Pb and Zn) in the Soils Adjacent to Streets of Lublin 69

Małgorzata KONCEWICZ-BARAN and Krzysztof GONDEK – Zinc, Cadmium and Lead Binding by Humus in Soil Fertilized with Composts 77

Ewa KRZYWY-GAWROŃSKA and Krystyna PRZYBULEWSKA – Evaluation of the Direct Effect and After-Effect of Organic Fertilisation without and with PRP Sol Addition on Soil Enzymatic Activity 87

Krzysztof KUD and Leszek WOŹNIAK – Selected Trace Elements in Soil and Plants from Marshy Meadows of the San River Valley 97

Stanisław MERCIK and Wojciech STĘPIEŃ – Effect of Nitrogen on Crop Yield as Influenced by Soil pH and Fertilization with Farmyard Manure 105

Marcin NIEMIEC, Barbara WIŚNIOWSKA-KIELIAN and Monika ARASIMOWICZ – Contents of Copper, Nickel and Chromium in the Sediments of Rainwater Reservoirs Situated Along the National Road No. 4 113

Magdalena SENZE and Monika KOWALSKA-GÓRALSKA – Presence of Metals in Waters from Sacred Springs in Europe 123

Urszula PANKIEWICZ – Monitoring of Total Mercury Level in Selected Dairy Products from the South-East Regions of Poland 129

Sebastian WERLE – Analysis of the Possibility of the Sewage Sludge Thermal Treatment 137

Katarzyna STEPANOWSKA, Marcin BIERNACZYK, Artur OPANOWSKI and Zbigniew NEJA – Selected Morphometric Characters, Condition, and Body Chemical Composition of Perch (*Perca fluviatilis* L.) from Lake Miedwie, Poland 145

Barbara SKWARYŁO-BEDNARZ – Influence of Contamination of Soil with Copper on the Activity of Dehydrogenases in Areas where Amaranthus is Cultivated 155

Katarzyna GRATA – Effect of Urea Phosphate on the *Bacillus* sp. Population in Soil and Antifungal Activity of Selected Strains on *Fusarium* sp. 161

Iwona ZAWIEJA, January BIEŃ and Małgorzata WORWĄG – Recovery of Volatile Fatty Acids During the Process of Anaerobic Stabilization of Sewage Sludge Coming from the Food Industry 169

VARIA

Invitation for ECOpole ’12 Conference 179

Guide for Authors 181

SPIS TREŚCI

Jolanta JONIEC i Jadwiga FURCZAK – Liczebność i aktywność wybranych grup mikroorganizmów, czynnych w przemianach węgla w glebie bielicowej wzbogaconej osadem ściekowym 7

Bogdan SZOSTAK – Zanieczyszczenia chemiczne gleby i wody w obejściu ferm trzody chlewnej 25

Jean B. DIATTA – Zastosowanie wskaźników geochemicznych do oceny zanieczyszczenia ołowiem i kadmem w rekreacyjnych parkach Poznania 35

Ireneusz GRZYWNOWICZ – Możliwości rolniczego zagospodarowania produktów odpadowych z działalności poszukiwawczo-wiertniczych 45

Anna IŻEWSKA, Justyna CHUDECKA, Tomasz TOMASZEWICZ i Mariola WRÓBEL – Zawartość makro- i mikroskładników w wierzchniej warstwie pobocza dróg terenów leśnych oraz charakterystyka gatunków roślin je zasiedlających 53

Monika JAKUBUS, Zbigniew KACZMAREK i Agnieszka WOLNA-MARUWKA – Zmiany wybranych właściwości gleby inkubowanej z dodatkiem agaru, skrobi i efektywnych mikroorganizmów 61

Andrzej PLAK, Piotr BARTMIŃSKI i Ryszard DĘBICKI – Niektóre prawidłowości w akumulacji i migracji metali ciężkich (Cd, Cu, Pb i Zn) w glebach sąsiadujących z ulicami Lublina 69

Małgorzata KONCEWICZ-BARAN i Krzysztof GONDEK – Wiązanie cynku, kadmu i ołowiu przez próchnicę w glebie nawożonej kompostami 77

Ewa KRZYWY-GAWROŃSKA i Krystyna PRZYBULEWSKA – Ocena bezpośredniego i następczego działania nawożenia organicznego bez i z dodatkiem PRP Sol na aktywność enzymatyczną gleby 87

Krzysztof KUD i Leszek WOŹNIAK – Wybrane mikroelementy w glebach i roślinach łąk łęgowych doliny Sanu 97

Stanisław MERCIK i Wojciech STĘPIEŃ – Działanie azotu na plonowanie roślin w zależności od odczynu gleby oraz nawożenia obornikiem 105

Marcin NIEMIEC, Barbara WIŚNIOWSKA-KIELIAN i Monika ARASIMOWICZ – Zawartość miedzi, niklu i chromu w osadach zbiorników wód deszczowych usytuowanych wzdłuż drogi krajowej nr 4 113

Magdalena SENZE i Monika KOWALSKA-GÓRALSKA – Obecność metali w wodach ze świętych źródeł w Europie 123

Urszula PANKIEWICZ – Monitoring poziomu rtęci całkowitej w wybranych produktach mleczarskich z regionów południowo-wschodniej Polski 129

Sebastian WERLE – Analiza możliwości energetycznego wykorzystania osadów ściekowych 137

Katarzyna STEPANOWSKA, Marcin BIERNACZYK, Artur OPANOWSKI i Zbigniew NEJA – Wybrane cechy morfometryczne, kondycja oraz skład chemiczny ciała okoni (*Perca fluviatilis* L.) z jeziora Miedwie, Polska 145

Barbara SKWARYŁO-BEDNARZ – Wpływ zanieczyszczenia gleby miedzią na aktywność dehydrogenaz pod uprawą amarantusa 155

Katarzyna GRATA – Wpływ fosforanu mocznika na liczebność bakterii z rodzaju *Bacillus* w glebie i aktywność przeciwgrzybową wybranych szczepów na *Fusarium* sp. 161

Iwona ZAWIEJA, January BIEŃ i Małgorzata WORWĄG – Pozyskiwanie lotnych kwasów tłuszczowych w procesie stabilizacji beztlenowej osadów pochodzących z przemysłu spożywczego 169

VARIA

Invitation for ECOpole ’12 Conference 179

Guide for Authors 181

DOI: 10.2428/ecea.2012.19(01)001 ECOL CHEM ENG A. 2012;19(1-2):7-24

Jolanta JONIEC[1] and Jadwiga FURCZAK[2]

NUMBERS AND ACTIVITY OF SELECTED MICROBIAL GROUPS INVOLVED IN CARBON TRANSFORMATIONS IN PODZOLIC SOIL AMENDED WITH SEWAGE SLUDGE

LICZEBNOŚĆ I AKTYWNOŚĆ WYBRANYCH GRUP MIKROORGANIZMÓW, CZYNNYCH W PRZEMIANACH WĘGLA W GLEBIE BIELICOWEJ WZBOGACONEJ OSADEM ŚCIEKOWYM

Abstract: Laboratory experiments were conducted in two variants, on a podzolic soil amended with the following doses of municipal-industrial sewage sludge: 30 Mg $\cdot$ ha^{-1} (1 %), 75 Mg $\cdot$ ha^{-1} (2.5 %), 150 Mg $\cdot$ ha^{-1} (5 %), 300 Mg $\cdot$ ha^{-1} (10 %) and 600 Mg $\cdot$ ha^{-1} (20 %). In one of the variants non-sterile sludge was applied, and in the other variant the sludge applied had been subjected to the process of sterilisation in order to determine the contribution of the sludge microorganisms in the transformation of organic matter. After 0.5, 1, 2, 3, 4 and 5 months from the application of the sludge, analyses were performed to determine the following parameters in the soils of the two variants: so-called total number of bacteria with low nutritional requirements, so-called total number of bacteria with high nutritional requirements, total number of filamentous fungi, number of cellulolytic fungi, respiratory activity, intensification of the process of cellulose mineralisation, and dehydrogenases activity. The analyses revealed that the non-sterile sewage sludge caused a stimulation of both the growth and the level of activity of the bacterial and fungal groups under study. That effect was usually the strongest at the beginning of the experiment and increased with increase in the dose of sludge applied. The non-sterile sludge had a stronger effect only on mineralisation of cellulose and on dehydrogenases activity, which may indicate participation of sludge microorganisms in those processes.

Keywords: soil, sterile and non-sterile sewage sludge, bacteria, fungi, respiration, cellulose mineralisation, dehydrogenases.

The extensive literature on the effect of sewage sludge on microbiological activity, and especially on biochemical activity related with carbon transformations in soils

---

[1] Institute of Environmental Engineering, Catholic University of Lublin, Off-Campus Faculty of Social Sciences in Stalowa Wola, ul. Ofiar Katynia 6a, 37–450 Stalowa Wola, Poland, phone: +48 15 642 25 42, email: jolajoniec1@gmail.com

[2] Faculty of Agricultural Microbiology, University of Life Science in Lublin, Leszczyńskiego 7, 20–069 Lublin, Poland, phone: +48 81 524 81 43, email: jadwiga.Furczak@up.lublin.pl

under laboratory conditions, demonstrates that the subject matter has frequently been the object of research [1–8]. The studies reported demonstrated a positive effect of sewage sludge both on the growth of microorganisms and on the processes that take place in soil with their participation. It should be emphasised, however, that the authors of those studies focused on a limited number of parameters, and primarily on the respiratory and dehydrogenases activity of soil [1, 6–8]. Therefore, it was considered worthwhile to conduct a broader study on the subject, using a larger number of tests, which would permit a more comprehensive assessment of the effect of sewage sludge on the biology of soil. Moreover, the study presented herein was also to provide an answer to the question to what extent microorganisms introduced in the soil with the sludge cooperate with the soil microorganisms in carbon transformation of organic matter and how long their activity persists. This issue has not been devoted much attention so far. Only Bonmati et al [9] addressed the problem, but their study was concentrated on microbiological transformations of nitrogen and phosphorus in soil amended with sewage sludge.

Materials and methods

The experiments were performed with a podzolic soil developed from weakly loamy sand, taken from the Ap horizon. Selected physical, physicochemical and chemical properties of the soil and of the sewage sludge are presented in Table 1 after Baran et al [10], Baran et al [11] and Oleszczuk and Baran [12]. In conformance with procedures commonly applied in studies of this type, prior to its application air-dry sewage sludge was crushed and screened through a sieve with 0.75 mm mesh. The laboratory experiment was set up in two variants. In one of them non-sterile sewage sludge from the Mechanical-Biological Sewage Treatment Plant in Konskie was added to 1 kg weighed portions of soil screened through a sieve with 2 mm mesh, at the following doses: 30 $\mathrm{Mg \cdot ha^{-1}}$ (1 %), 75 $\mathrm{Mg \cdot ha^{-1}}$ (2.5 %), 150 $\mathrm{Mg \cdot ha^{-1}}$ (5 %), 300 $\mathrm{Mg \cdot ha^{-1}}$ (10 %) and 600 $\mathrm{Mg \cdot ha^{-1}}$ (20 %) of dry matter. In the second variant, the same doses of the sludge were applied, but prior to the application the sludge was thermally sterilised. The sterilisation of the sludge was done in an autoclave (30 min. 0.1 HPa), three times at 24 hour intervals [9].

After the addition of the sludge, all soil samples were wetted to about 60 % t.w.c. and incubated at room temperature for a period of 5 months, maintaining soil moisture at a more or less constant level. The control treatment in the experiment was soil with no sewage sludge addition.

Microbiological and biochemical analyses and determinations of the soil reaction were made after 0.5, 1, 2, 3, 4 and 5 months of the experiment duration, while those for the sludge were performed only once, prior to the start of the experiment. At the beginning of the experiment and after 5 months from the introduction of the non-sterile sludge in the soil determinations of the total carbon content in the soil were made as well.

Within the scope of the experiment, determinations were made of the so-called total number of bacteria with low nutritional requirements, on a medium with soil or sludge extract (350 cm · dm^{-3}) and K_2HPO_4, of so-called total number of bacteria with high nutritional requirements, on Bunt–Rovira medium [13], of so-called total number of filamentous fungi, on Martin medium [14], of the numbers of cellulolytic fungi, on mineral agar covered with a circle of Whatman paper with an addition of antibiotic sin accordance with Martin's recommendations [14], of the respiratory activity, with the method of Rühling et al [15], of the rate of cellulose mineralisation, in 25-gram weight portions of the soil enriched with 0.5 % of powdered Whatman celulose, and the amount of CO_2 emitted from them during 20 days was determined with the method of Ruhling et al [15], of dehydrogenases activity, with the Thalmann method [16], of reaction, potentiometrically in 1mol · dm^{-3} KCl, and of organic carbon content, with the method of Tiurin as modified by Simakov.

Table 1

Properties of the soil and sewage sludge used in the field experiment

Properties	Unit		Soil	Sludge
Granulometric composition	% of fraction [mm]	1–01 0.1–0.02 < 0.02	86 7 7	
pH	1 mol · dm $^{-3}$ KCl		6.0	6.4
T	mmol (+) · kg^{-1}		71.3	607.7
$C_{organic}$ (C_{org})	g · kg $^{-1}$		11.2	210.0
N_{total} (N_t)			1.4	17.8
C_{org}: N_t	[-]		7.9	11.8
Cd content	mg · kg^{-1}		0.5	6.0
Cu content			7.0	216.0
Pb content			18.6	125.0
Sum of 16 PAHs	μg· kg^{-1}		43.0	3894.0

All determinations of microbiological and biochemical parameters were made in three replications. The results were processed statistically with the method of analysis of variance. The significance of differences was determined with the Tukey test at $p = 0.05$. Moreover, means for the period of the experiment were plotted on graphs as percentages of increase or decrease, adopting mean values obtained for the control soil as 100 %.

Results and discussion

The sterile or non-sterile sludge introduced in the soil caused a significant stimulation of the number of bacteria with low nutritional requirements (Table 2). Comparing the effect of the two types of sludge it should be emphasised that the sterile sludge exerted a stronger impact in this respect, as in treatments with that sludge applied the numbers of those bacteria were notably greater. This constitutes a basis for the formulation of a thesis that there exists a negative interaction between microorganisms introduced with the sludge and oligotrophic soil bacteria. In both variants of the experiment the stimulation was more pronounced in treatments with the higher doses of the sludge.

Table 2

Selected properties of microbiological, biochemical and chemical sewage sludge

Oligotrophic bacteria, cfu $\cdot 10^9 \cdot kg^{-1}$dm of sludge	28.7
Macrotrophic bacteria, cfu $\cdot 10^9 \cdot kg^{-1}$dm of sludge	77.1
Filamentous fungi, cfu $\cdot 10^6$ kg^{-1} dm of sludge	1050.5
Cellulolytic fungi, cfu $\cdot 10^6 \cdot kg^{-1}$ dm of sludge	0.0
Respiratory activity, mg C-$CO_2 \cdot kg^{-1}$ dm of sludge $\cdot d^{-1}$	1590.0
Cellulose mineralization, mg C-$CO_2 \cdot kg^{-1}$ dm of sluge $\cdot$ 20 d^{-1}	74653.3
Dehydrogenases activity, mg TPF $\cdot kg^{-1}$ dm of sludge $\cdot d^{-1}$	95.0
Cellulose, % air dm of sludge	6.6

The observed stimulation of the growth of those bacteria was characterised, in both experimental variants, by a certain dynamics of changes over the period studied (Table 2). In the initial phase of the experiment (after 0.5 month) the stimulating effect of the sludge was the weakest. Subsequently, the effect of the sludge on the numbers of those bacteria gradually intensified, attaining the highest level after 2 and 3 months. In the final phase of the experiment (4 and 5 months) the effect of the sludge was notably reduced, which was most likely related with deterioration of the living conditions of the bacteria.

Stimulating effect of non-sterile sewage sludge on the growth of the bacterial group in question was also observed in laboratory studies by Furczak and Joniec [2] and by Kobus et al [3]. Those authors, as in the study presented here, observed a relation of those changes to the sludge dose applied and to the duration of the sludge effect on the soil. Another factor that appears to cause intensified multiplication of that bacterial group in soil amended with sewage sludge is increase in the soil reaction (Table 3).

Table 3

Reaction of soil (pH_{KCl})

Treatments		Terms of analyses, months					
		0.5	1	2	3	4	5
Control soil		6.1	6.0	6.0	5.9	6.0	6.0
Soil + 1 % of sludge	Series with non-sterile sludge	6.0	6.0	5.7	5.6	5.7	5.8
Soil + 2.5 % of sludge		6.6	6.7	6.3	6.1	5.9	6.1
Soil + 5 % of sludge		6.8	6.6	6.6	6.3	6.1	6.2
Soil + 10 % of sludge		6.9	6.8	6.5	6.6	6.5	6.5
Soil + 20 % of sludge		6.9	6.5	6.5	6.6	6.5	6.6
Soil + 1 % of sludge	Series with sterile sludge	7.0	6.6	5.8	6.5	6.4	6.5
Soil + 2.5 % of sludge		7.0	6.8	6.7	6.5	6.3	6.4
Soil + 5 % of sludge		7.1	6.8	6.6	6.5	6.5	6.5
Soil + 10 % of sludge		7.1	6.7	6.7	6.6	6.6	6.7
Soil + 20 % of sludge		7.0	6.6	6.5	6.6	6.7	6.8

These observations are supported by earlier studies by Hattori and Hattori [17] which showed that some oligotrophic bacteria, in spite of their low nutritional requirements, have a capacity to live in environments with a high concentration of nutrients. Also Wielgosz [18] noted an abundant occurrence of bacteria with low nutritional requirements in sewage sludge, which could partially support the results of our study. Data in Table 4 indicate that also the sludge used in this experiment introduced a certain pool of those bacteria to the soil. However, weaker growth of bacteria with low nutritional requirements in the soil with non-sterile sludge than in than with sterile sludge indicates that bacteria from the sludge rather did not colonise the soil environment. It is to be supposed that there may have appeared the phenomenon of competition between the microbial groups introduced with the sludge and the soil microorganisms, which led to an inhibition of the growth of the bacterial group under study.

Table 4

C-organic content (C_{org}) [$g \cdot kg^{-1}$]

Treatments	Terms of analyses, months	
	0.5	5
Control soil	7.32	6.48
Soil + 1 % of sludge	8.16	5.60
Soil + 2.5 % of sludge	11.04	10.24
Soil + 5 % of sludge	14.88	12.40
Soil + 10 % of sludge	22.08	20.16
Soil + 20 % of sludge	32.40	29.52

The data in Table 5 indicate that both types of sewage sludge also had a stimulating effect on the growth of bacteria with high nutritional requirements. That effect was generally more distinct and more significant in the presence of higher concentrations of the sludge. The observed stimulation became apparent at the beginning of the experiment (after 0.5 month) more strongly than in the case of oligotrophic bacteria. In both variants of the experiment the most intensive growth of that group of bacteria occurred during the first two months of the experiment. Subsequently the effect of the sludge became slightly weaker and was statistically significant only in treatments with the higher doses of the sludge.

A positive effect of non-sterile sewage sludge on the growth of macrotrophic bacteria in soil under laboratory conditions was observed also by Lima et al [5].

The stimulation observed in this experiment was probably induced by the supply, with the sludge, of a large amount of nutrients necessary for the growth of those bacteria. This is supported by the results presented in Table 6 that indicate an increase in organic carbon content in the soil following the application of the sludge. Another factor that appears to cause, to a degree, intensified multiplication of that bacterial group in soil in treatments with higher doses of the sewage sludge was surely an increase in the soil reaction (Table 3).

It appears that, as in the case of oligotrophic bacteria, also sludge bacteria with high nutritional requirements did not colonise the soil environment, and even the microorganisms brought in with the sludge could have contributed to a reduction in the

Table 5

Total number of oligotrophic bacteria, cfu · 10^9 · kg^{-1} dm of soil

Treatments		Terms of analyses, months						Mean for treatments	Mean for dose	Mean for kind of sludge
		0.5	1	2	3	4	5			
Control soil		20.0	1.7	1.0	1.3	2.2	3.9	5.0	5.0	16.0
Soil + 1 % of sludge	Series withnon-sterile sludge	26.4	9.4	6.6	13.4	7.7	17.3	13.7	14.8	
Soil + 2.5 % of sludge		29.5	14.0	18.8	19.0	13.3	23.7	20.0	26.2	
Soil + 5 % of sludge		26.7	22.3	15.9	17.7	5.8	20.0	18.0	25.3	
Soil + 10 % of sludge		49.0	14.2	16.9	28.6	9.5	18.0	22.8	37.4	
Soil + 20 % of sludge		8.9	7.1	13.3	22.0	13.4	33.9	16.4	30.7	
Soil + 1 % of sludge	Series with sterile sludge	8.0	18.3	20.3	16.3	12.2	20.7	16.0		30.5
Soil + 2.5 % of sludge		21.3	29.5	34.4	48.0	34.2	27.8	32.4		
Soil + 5 % osadu		42.7	29.6	35.6	32.4	35.9	21.7	32.7		
Soil + 10 % of sludge		70.4	21.7	58.0	38.6	53.7	63.8	52.1		
Soil + 20 % of sludge		64.2	52.7	32.3	33.0	21.3	64.5	44.9		
Mean for term		32.0	18.5	21.1	22.6	18.6	26.6			

$LSD_{(0.05)}$ ($NIR_{(0.05)}$): term (T) – 2.1; sterility (S) – 0.8; dose (D) – 2.1
Interactions: T x S – 3.5; T x D – 6.5; S x D – 3.5; T x S x D – 9.2

Table 6

Total number of macrotrophic bacteria, cfu · $10^9 \cdot kg^{-1}$ dm of soil

Treatments		Terms of analyses, months						Mean for treatments	Mean for dose	Mean for kind of sludge
		0.5	1	2	3	4	5			
Control soil		3.8	2.9	3.1	7.2	5.0	3.9	4.3	4.3	21.1
Soil + 1 % of sludge	Series with non-sterile sludge	22.3	12.7	29.1	5.9	18.0	15.9	17.3	19.8	
Soil + 2.5 % of sludge		20.6	12.5	22.5	15.2	20.3	13.6	17.5	27.9	
Soil + 5 % of sludge		39.3	19.0	33.0	13.2	27.2	30.5	27.0	37.6	
Soil + 10 % of sludge		49.4	24.5	10.0	28.2	26.4	28.6	27.8	51.4	
Soil + 20 % of sludge		34.9	19.5	40.3	28.4	37.7	33.9	32.4	63.4	
Soil + 1 % of sludge	Series with sterile sludge	26.3	21.2	31.7	14.1	26.3	13.7	22.2		47.0
Soil + 2.5 % of sludge		45.8	35.3	44.5	47.2	29.8	27.8	38.4		
Soil + 5 % of sludge		65.2	50.3	41.7	32.4	38.8	59.9	48.1		
Soil + 10 % of sludge		114.1	12.7	78.5	68.7	98.4	77.2	74.9		
Soil + 20 % of sludge		155.6	69.7	83.4	47.6	121.9	87.9	94.3		
Mean for term		48.1	23.6	35.1	26.3	37.9	33.1			

$LSD_{(0.05)}$ ($NIR_{(0.05)}$): T – 3.4; S – 1.4; D – 3.4
Interactions: T x S – 5.6; T x D – 10.4; S x D – 5.6; T x S x D – 14.8
Explanations as in Table 5.

number of soil bacteria of this type. This is indicated by the higher number of the bacteria in question in the soil with the sterile sludge (Table 5). The stronger stimulation of the growth of that bacterial group in the soil with sterile sludge could have been caused by the provision of an additional source of organic matter, in the form of microorganisms decayed through the process of sterilisation of the sludge. This supposition is also supported by earlier studies conducted by Sastre et al [19].

Amendment of the soil with the non-sterile and sterile sludge caused also an increase in the total number of filamentous fungi (Table 7). That effect, however, was statistically proven only in treatments with the higher doses of the waste.

The positive effect of the sludge on the growth of the fungi was the most apparent after 2 weeks from the time of sludge application, then it grew weaker and until the end of the experiment remained at a lower level (Table 7).

This study supports the observations of, among others, Kobus et al [3] and Lima et al [5], indicating increased numbers of fungi in soil amended with sewage sludge.

In the opinion of many authors, among others Kobus et al [3] and Sastre et al [19], it is common knowledge that microbiological activity of soils depends on their content of organic matter. As sewage sludge abounds in various organic substances, it appears that the primary cause of the stimulation of fungal growth observed in this study was, as in the case of bacteria, enrichment of the soil in nutrients. This is indicated by the increase in organic carbon content in the soil, caused by the introduction of the sludge (Table 6). The fundamental effect of organic matter on the stimulation of fungal growth is supported by the fact that the effect appeared in spite of the soil reaction increase (Table 3) to a level close to the neutral. Data in Table 4 indicate that filamentous fungi are present in the sludge applied only at a slight level. This accounts for the lack of notable differences in the growth of those microorganisms between the analysed series of the experiment (Table 7).

The data given in Table 8 inform that the higher doses of the sterile and non-sterile sewage sludge (10 and 20 %) caused a visible, statistically proven, stimulation of the growth of cellulolytic fungi. In treatments with lower concentrations of the sludge, however, only a slight tendency towards an increase in the numbers of the microbial group in question was noted. The positive effect of the sludge on the microbiological parameter under consideration was the most apparent after 0.5, 3, 4 and 5 months (Table 8). Whereas, on the other dates of analyses it was insignificant and oscillated around a level similar to that of the control treatment.

The somewhat stronger growth of cellulose-decomposing fungi in the soil with sterile sludge than in that with non-sterile sludge may indicate a certain unfavourable effect of the sludge microorganisms (Table 8). Apparently it was primarily the cellulose and other nutrients for that microbial group, introduced with the sludge, that contributed to the growth of the number of cellulolytic fungi observed in this study. The results obtained support an earlier laboratory study by Furczak and Joniec [2], concerning the effect of the degree of fragmentation of sewage sludge on microbiological and biochemical properties of soil, that revealed an increase in the numbers of cellulose-decomposing fungi in soil amended with sewage sludge.

Table 7

Total number of filamentous fungi, cfu · 10^6 · kg^{-1} dm of soil

Treatments		Terms of analyses, months						Mean for treatments	Mean for dose	Mean for kind of sludge
		0.5	1	2	3	4	5			
Control soil		19.6	28.2	30.0	17.7	8.4	44.9	24.8	24.8	46.6
Soil + 1 % of sludge	Series with non-sterile sludge	42.7	49.0	36.6	24.1	22.4	52.0	37.8	32.8	
Soil + 2.5 % of sludge		37.0	29.1	39.8	25.5	3.0	58.1	32.1	38.6	
Soil + 5 % of sludge		93.0	38.0	76.1	30.7	8.6	87.1	55.6	46.5	
Soil + 10 % of sludge		77.4	81.5	99.6	52.8	26.8	38.1	62.7	60.4	
Soil + 20 % of sludge		126.3	51.9	114.4	41.1	16.6	51.0	66.9	67.5	
Soil + 1 % of sludge	Series with sterile sludge	33.7	28.8	31.0	21.1	1.1	51.0	27.8		43.5
Soil + 2.5 % of sludge		71.6	47.2	51.3	14.6	11.8	73.7	45.0		
Soil + 5 % of sludge		59.1	60.4	31.0	32.0	8.6	33.6	37.5		
Soil + 10 % of sludge		107.9	64.8	54.8	53.8	11.3	55.4	58.0		
Soil + 20 % of sludge		128.9	102.1	46.7	54.3	6.7	70.1	68.1		
Mean for term		68.1	50.8	53.5	32.1	11.1	55.0			

$LSD_{(0.05)}$ ($NIR_{(0.05)}$): T – 4.1; S – 1.6; D – 4.1
Interactions: T x S – 6.7; T x D – 12.5; S x D – 6.7; T x S x D – 17.7
Explanations as in Table 5.

Table 8

Population of cellulolytic fungi, cfu · 10^6 · kg^{-1} dm of soil

Treatments		Terms of analyses, months						Mean for treatments	Mean for dose	Mean for kind of sludge
		0.5	1	2	3	4	5			
Control soil		2.1	2.3	2.9	2.2	2.2	2.4	2.3	2.3	12.8
Soil + 1 % of sludge	Series with non-sterile sludge	3.9	2.7	1.7	2.2	5.9	3.6	3.3	2.8	
Soil + 2.5 % of sludge		3.4	3.8	1.9	4.0	2.7	4.3	3.3	4.1	
Soil + 5 % of sludge		19.4	3.4	1.6	6.1	2.3	4.8	6.3	6.2	
Soil + 10 % of sludge		34.2	3.4	5.4	60.8	55.9	7.5	27.9	28.9	
Soil + 20 % of sludge		58.2	5.5	5.4	68.6	48.2	17.1	33.8	34.9	
Soil + 1 % of sludge	Series with sterile sludge	2.4	3.6	1.1	2.7	2.0	2.1	2.3		13.6
Soil + 2.5 % of sludge		3.2	2.4	1.9	5.9	13.2	2.8	4.9		
Soil + 5 % osadu		4.1	3.4	2.7	21.7	1.9	2.8	6.1		
Soil + 10 % of sludge		40.6	5.4	2.6	28.5	97.2	4.9	29.9		
Soil + 20 % of sludge		63.0	5.4	3.6	96.5	40.1	7.4	36.0		
Mean for term		19.7	3.6	2.8	25.1	22.8	5.2			

$LSD_{(0.05)}$ ($NIR_{(0.05)}$): T – 2.0; S – no significant differences; D – 2.0
Interactions: T x S – 3.2; T x D – 6.1; S x D – no significant differences; T x S x D – 8.6
Explanations as in Table 5.

The data presented in Table 9 show that both the sterile and the non-sterile sewage sludge caused a generally significant increase in the respiratory activity of the soil. The stimulation usually increased with increase in the sludge dose, assuming the highest values in the treatments with 10 and 20 % of the waste. The sterile sludge caused a significantly stronger stimulation of carbon mineralisation than the non-sterile sludge. The stronger stimulation of the respiratory processes by the sterile sludge was most likely a result of increase in the amount of respiration substrata, brought into the soil with the sludge microorganisms killed in the process of sludge sterilisation, and of the lack of competition.

During the 5 months of the experiment, the effect of the sludge on the emission of CO_2 varied in intensity (Table 9). A significant stimulating effect of all the doses of the sludge was observed only at the beginning of the experiment, *ie* after 0.5 and 1 month. The stimulation of respiratory activity noted after 2 months was the strongest, though it was statistically substantiated only from the second dose of the sludge, *ie* 2.5 %, upwards. On the successive dates of analyses (3 and 4 months) the stimulating effect of the sludge was generally reduced, and in the final phase of the experiment it was almost non-observable. The weakening of the effect of the sludge on the process analysed with the passage of time was probably due to the exhaustion of the more readily available respiration substrates. Similar conclusions were proposed by Debosz et al in their study [1].

Stimulation of the respiratory activity of soil by sewage sludge is indicated by numerous laboratory studies [1, 2, 6, 8]. Moreover, Saviozzi et al [8] observed, as we did in this study, a dependence of the intensity of that effect on the level of sludge dose applied, while Debosz et al [1] observed a weakening of the effect with the passage of time, that even turned to inhibition in the final phase of the experiment.

The amount of CO_2 emitted from soils primarily depends on the activity of microorganisms inhabiting it [20]. In the opinion of Hattori and Mukai [21], intensification of the processes of mineralisation of organic carbon depends primarily on the level and quality of organic matter. Therefore, it seems that the observed stimulation of respiration was caused first of all by the supply of a large amount of carbon organic matter to the soil with the sewage sludge, that organic matter being a source of respiratory substrates for microorganisms. This is indicated by the increase in the content of organic carbon in the soil amended with the waste (Table 6). Another factor that contributed to the stimulation of CO_2 emission could also be an increase in the soil reaction (Table 3) that was conducive to the growth of bacteria. As it is known, the role of bacteria in the mineralisation of organic matter is greater than that of fungi. The results given in Table 4 inform that numerous microorganisms get in the soil together with sewage sludge. However, in the experimental series with the non-sterile sludge there may have taken place an unfavourable interaction between the indigenous soil microorganisms and those introduced with the sludge. This mainly related to bacteria (Tables 2, 5), the result of which was lower stimulation of respiratory processes under those conditions (Table 9).

The sterile and non-sterile sewage sludge introduced in the soil caused also a significant intensification of cellulose mineralisation (Table 10). That stimulation corresponded with the dose of the waste, attaining, as in the case of respiratory activity,

Table 9

Respiratory activity, mg $C\text{-}CO_2 \cdot kg^{-1}$ dm of soil $\cdot\ d^{-1}$

Treatments		Terms of analyses, months						Mean for treatments	Mean for dose	Mean for kind of sludge
		0.5	1	2	3	4	5			
Control soil		159.0	294.0	31.0	65.5	23.0	102.0	112.5	112.5	260.0
Soil + 1 % of sludge	Series with non-sterile sludge	402.5	517.0	115.5	95.5	35.5	83.0	208.0	201.0	
Soil + 2.5 % of sludge		454.5	547.0	126.0	148.5	72.0	67.0	235.0	280.0	
Soil + 5 % of sludge		505.5	556.0	210.5	312.5	62.0	118.0	277.5	331.5	
Soil + 10 % of sludge		621.5	593.0	254.5	243.0	211.0	95.5	336.5	414.0	
Soil + 20 % of sludge		655.5	678.0	339.5	353.5	154.5	158.0	390.0	437.5	
Soil + 1 % of sludge	Series with sterile sludge	342.0	469.5	136.0	139.0	25.5	52.0	194.0		332.0
Soil + 2.5 % of sludge		536.0	585.5	244.0	268.0	166.0	148.0	324.5		
Soil + 5 % osadu		636.0	576.0	364.5	360.0	244.0	134.5	386.0		
Soil + 10 % of sludge		811.5	682.0	452.5	455.5	324.0	223.0	491.5		
Soil + 20 % of sludge		956.0	740.0	382.5	374.5	298.5	159.5	485.5		
Mean for term		520.0	544.5	224.0	231.5	136.5	120.0			

$LSD_{(0.05)}$ ($NIR_{(0.05)}$): T –21.5; S –8.5; D –21.5
Interactions: T x S –35.0; T x D –65.5; S x D –35.0; T x S x D – 92.5
Explanations as in Table 5.

Table 10

Cellulose mineralization, mg C-CO$_2$ · kg^{-1} dm of soil · 20 d^{-1}

Treatments		Terms of analyses, months						Mean for treatments	Mean for dose	Mean for kind of sludge
		0.5	1	2	3	4	5			
Control soil		147.2	1550.4	1667.6	1872.8	1370.0	1442.4	1562.4	1562.4	2952.8
Soil + 1 % of sludge	Series with non-sterile sludge	2986.0	2341.2	2193.6	2022.4	1426.8	950.4	1986.8	2088.0	
Soil + 2.5 % of sludge		4649.0	3674.0	2757.6	2657.2	1646.8	1958.4	2735.6	2399.2	
Soil + 5 % of sludge		3876.8	4112.0	3990.8	2440.0	1778.0	1118.4	2886.0	2681.6	
Soil + 10 % of sludge		4846.4	5420.0	5508.4	3824.4	3524.8	1360.0	4080.8	3870.8	
Soil + 20 % of sludge		6133.2	5956.4	6474.8	4698.4	2162.4	1362.8	4464.8	4336.4	
Soil + 1 % of sludge	Series with sterile sludge	3432.8	2208.4	2423.2	1972.8	1716.0	1379.6	2189.2		2693.6
Soil + 2.5 % of sludge		3893.6	1502.4	2126.0	2129.6	1550.0	1176.8	2063.2		
Soil + 5 % osadu		4746.4	2267.2	2954.0	1999.2	1459.2	1427.6	2477.2		
Soil + 10 % of sludge		4693.6	3860.4	5222.0	3430.0	3344.0	1412.8	3660.4		
Soil + 20 % of sludge		6992.0	4482.4	3394.4	6071.6	3641.2	1665.2	4207.6		
Mean for term		4022.0	3243.6	3372.0	2916.0	2000.0	1391.6			

LSD$_{(0.05)}$ (NIR$_{(0.05)}$): T –126.0; S–50.0; D– 126.0
Interactions: T x S –204.4; T x D –384.0; S x D –204.4; T x S x D –543.2
Explanations as in Table 5.

the highest level in treatments with 10 and 20 % sludge content. The relation of the rate of cellulose mineralisation to the concentration of sewage sludge in the soil was also noted in laboratory conditions by Furczak and Joniec [2], studying the effect of the degree of sludge fragmentation on that process. As in this study, that effect became weaker with the passage of time. The data given in Table 10 indicate that the stimulating effect of sewage sludge on the process of cellulose mineralisation was the strongest on the first three dates of analyses, ie after 0.5, 1 and 2 months. The observed stimulation grew weaker with the passage of time, that phenomenon being more rapid in soil with the lower doses of the sludge (1, 2.5 %). Therefore, on subsequent dates of analyses (3 and 4 months) the stimulation of the process of cellulose mineralisation was still clearly observable only in treatments with 10 and 20 % of the waste. Whereas, after 5 months no significant stimulating effect of the sludge on the parameter in question was observed any longer. In certain treatments there even appeared a slight, though not substantiated statistically, inhibition of the process of cellulose mineralisation.

Studies by Debosz et al [1] and by Hattori and Mukai [21] as well as the data given in Table 4 indicate that sewage sludge is a source of cellulose, among other things. Therefore, it should be supposed that the stimulation of the rate of cellulose mineralisation observed in our study was caused by the introduction of certain amounts of that polysaccharide, and other nutrients for that microbial group, into the soil together with the sewage sludge. Whereas, the decrease of the stimulation observed with the passage of time was most likely related with the exhaustion of the substrate due to the activity of cellulolytic microorganisms (Table 8). The observed higher intensity of the process of cellulose mineralisation in the soil with the non-sterile sludge (Table 10) could be attributed in part to the activity of cellulases of cells of cellulolytic bacteria brought in with the sludge (Table 4). A certain role in that complex process could also have been played by other heterotrophic microorganisms participating in the process of mineralisation of excess products of cellulose decomposition.

The results given in Table 11 indicate that the introduction of both the sterile and the non-sterile sewage sludge in the soil caused a stimulation of the soil dehydrogenase activity, generally increasing with increase in the dosage. That effect was statistically significant in almost all treatments, with the exception of that with the lowest dose of the waste (1 %).

The stimulation observed in this study was the most pronounced in the initial phase of the experiment, ie after 0.5 a month (Table 11), while on the second date of analyses (after 1 month) it weakened notably and remained on a similar level until the end of the experiment. The results of studies conducted so far in this area are not equivocal. Studies by numerous authors, conducted under laboratory conditions [2, 4, 6–8], indicate that in most cases sewage sludge has a positive effect on dehydrogenase activity of soils. Whereas, Kucharski et al [4], depending on the kind of sewage sludge applied, apart from the stimulation also observed an inhibition of the activity of the enzymes studied.

As in our study, usually a weakening of the stimulation of dehydrogenase activity with the passage of time was observed [6–8].

Table 11

Dehydrogenases activity, mg TPF · kg^{-1} dm of soil · d^{-1}

Treatments		Terms of analyses, months						Mean for treatments	Mean for dose	Mean for kind of sludge
		0.5	1	2	3	4	5			
Control soil		1.67	2.49	2.19	2.26	1.76	3.00	2.23	2.23	12.44
Soil + 1 % of sludge	Series with non-sterile sludge	4.67	5.23	2.46	3.67	3.31	5.63	4.16	4.02	
Soil + 2.5 % of sludge		7.28	8.42	5.49	5.15	3.70	8.04	6.35	6.09	
Soil + 5 % of sludge		13.89	11.48	7.29	13.01	3.85	10.18	9.95	10.19	
Soil + 10 % of sludge		30.23	28.10	17.18	14.52	10.46	24.54	20.84	18.89	
Soil + 20 % of sludge		50.13	40.13	7.83	35.35	18.28	35.05	31.13	27.28	
Soil + 1 % of sludge	Series with sterile sludge	3.94	2.98	2.90	2.82	3.30	7.39	3.89		10.46
Soil + 2.5 % of sludge		5.17	5.30	3.41	4.71	2.53	13.87	5.83		
Soil + 5 % osadu		11.40	10.36	22.26	7.05	4.01	7.46	10.42		
Soil + 10 % of sludge		25.90	20.26	12.98	9.65	6.15	26.75	16.95		
Soil + 20 % of sludge		48.42	18.08	17.80	16.62	11.44	28.26	23.44		
Mean for term		17.03	12.94	8.66	9.75	5.88	14.43			

LSD$_{(0.05)}$ (NIR$_{(0.05)}$): T – 0.91; S – 0.36; D – 0.91
Interactions: T x S – 1.48; T x D – 2.78; S x D – 1.48; T x S x D – 3.94
Explanations as in Table 5.

The activity of enzymes in soil is mostly the result of microbial activity [22]. Therefore, the stimulation of dehydrogenases activity (Table 11) was a reflection of the growth of the analysed bacterial and fungal groups that was observed in this study (Tables 2,5,7,8). In the opinion of many authors, dehydrogenases activity is strongly correlated with, among other things, the content of organic carbon in soil [23]. That observation is supported by this study which demonstrated an increase in the level of that biochemical parameter (Table 6). Another factor contributing to the stimulation of the activity of the enzymes in question could also be increase of pH in the soil with the sludge (Table 3) because**,** as reported by Chazijew [24] and by Quilchano and Maranon [25], there is a positive correlation between those parameters. In the opinion of Pascual et al [7], sludge organic matter additionally alleviates the negative effect of contaminants (eg heavy metals or toxic compounds of organic character), introduced with sewage sludge, on dehydrogenases activity. Sensitivity of dehydrogenases to heavy metals was reported by Moreno et al [26], among others.

With relation to that, the weakening of the stimulation of the activity of those enzymes, observed beginning with the second date of analyses, was probably caused by the depletion, with the passage of time, of the amount of available organic matter through its mineralisation, and therefore by an intensification of the negative effect of contaminants present in the sludge (Table 1). A progressing decrease in the level of organic matter is indicated by the results presented in Table 6.

The stimulating effect of the sterile sludge on dehydrogenases activity was, within the period studied, notably weaker than that of the non-sterile sludge (Table 11), which suggests that a certain role in the variation of that parameter could have been played by microorganisms coming from the sludge itself.

Summary and conclusions

1. In the soil with the non-sterile sludge almost all the sludge doses applied caused a stimulation of the growth of bacteria with low and high nutritional requirements and of filamentous fungi. That effect was stronger in treatments with the higher doses of the sludge (5, 10 and 20 %). The highest doses of the sludge caused also an increase in the number of cellulolytic fungi. The most intensive growth of bacteria with high nutritional requirements and of filamentous fungi occurred at the beginning of the experiment, of oligotrophic bacteria in the 2nd and 3rd months, and of cellulolytic fungi – at the beginning and in the 3rd and 4th months of the experiment. The experiments conducted in parallel with the sterile sludge suggest that bacteria from the sludge rather did not colonise the soil, and even there may have appeared unfavourable interactions between the soil bacteria and the microorganisms introduced with the sludge.

2. All doses of the non-sterile sewage sludge caused an intensification of the process of respiration, cellulose mineralisation, and of the dehydrogenases activity of the soil. That effect usually intensified with increase in the concentration of the waste in the soil. Respiration attained the highest values in the 2nd, 3rd and 4th months of the experiment, cellulose mineralisation – in the first two months, and dehydrogenases activity only at the beginning of the experiment, ie during the initial two weeks. The higher levels of

cellulose mineralisation and dehydrogenases activity in the soil amended with the non-sterile sludge may indicate a certain significant role of other microorganisms than those analysed in this study, ie those coming from the sludge itself, in those processes in the soil.

3. The observed relatively rapid decrease of the effect of the sewage sludge, under laboratory conditions as compared with field conditions [27], on the microbiological and biochemical parameters of soil under study, indicates a lower credibility and usefulness of laboratory experiments in the assessment of ecological effects of the introduction of the waste in soil.

References

[1] Debosz K, Petersen SO, Kure LK, Ambus P. App Soil Ecol. 2002;19:237-248. DOI: 10.1016/S0929-1393(01)00191-3.
[2] Furczak J, Joniec J. Polish J Soil Sci. 2002;35:59-67.
[3] Kobus J, Czaban J, Gajda A. Pamięt Puław – Prace IUNG. 1990;96:121-137.
[4] Kucharski J, Wyszkowska J, Nowak G, Harms H. Polish J Soil Sci. 2000;33:29-36.
[5] Lima J.A, Nahas E, Gomes AC. Appl Soil Ecol. 1996;4:75-82. DOI: 10.1016/0929-1393(96)00094-7.
[6] Moreno JL, Hernandez T, Perez A, Garcia C. Appl Soil Ecol. 2002;21:149-158. DOI: 10.1016/S0929-1393(02)00064-1.
[7] Pascual JA, Hernandez T, Garcia C, Ayuso M. Biores Techn. 1998;64:131-138. DOI: 10.1016/S0960-8524(97)00171-5.
[8] Saviozzi A, Bufalino P, Levi-Minzi R, Riffaldi R. Biol Fertil Soils. 2002;35:96-101. DOI: 10.1007/s00374-002-0445-9.
[9] Bonmati M, Pujola, Sana J, Soliva M, Felipo MT, Garau M, Ceccanti B, Nannipieri P. Plant and Soil. 1985;84:79-91. DOI: 10.1007/BFO2197869.
[10] Baran S, Bielińska EJ, Wójcikowska-Kapusta A. Folia Univ Agric Stetin. 2000;84:19-24.
[11] Baran S, Wójcikowska-Kapusta A, Milczarek T. Chem Agricult. 2003;4:461-468.
[12] Oleszczuk P, Baran S. Archives Environ Protect. 2004;30:35-50.
[13] Bunt JB, Rovira AD. Soil Sci. 1955;6:119-128.
[14] Martin J. Soil Sci. 1950;69:215-233.
[15] Rühling A, Tyler G. Oikos. 1973;24:402-415.
[16] Thalmann A. Landwirtsch Forsch. 1968;21:249-258.
[17] Hattori R, Hattori T. J Gen Appl Microbiol. 1980;26:1–14. DOI: 10.2323/jgam.26.1.
[18] Wielgosz E. Ann UMCS, sec E. 2000;55:169-184.
[19] Sastre J, Vincente MA, Lobo HC. Biores Techn. 1996;57:19–23. DOI: 10.1016/0960-8524(96)00035-1
[20] Kuzyakov Y. Soil Biol Biochem**.** 2006;38:425-448. DOI: 10.1016/j.soilbio.2005.08.020.
[21] Hattori H, Mukai S. Soil Sci Plant Nutr. 1986;32:421-432.
[22] Dick RP. Soil enzyme activities as indicators of soil quality. In: Doran JV, Coleman DC, Bezdicek DF, Stewart BA, editors. Defining soil quality for a sustainable environment. Soil Sci Soc Amer, Amer Soc Agric. Madison: 1994.
[23] Masciandaro G, Ceccanti B, Garcia C. Soil Biol Biochem. 2000;32:1015–1024. DOI: 10.10/SOO38-01717(00)00011-0
[24] Chazijew FCh. Sistemno-ekołogiczeskij analiz fiermentatiwnoj aktiwnosti poczw. Nauka, Moskwa: 1982.
[25] Quilchano C, Maranon T. Biol Fertil Soils. 2002;35:102–107. DOI: 10.1007/s00374-002-0446-8.
[26] Moreno JL, Garcia C, Hernandez T. Europ J Soil Sci. 2003;54:377–382. DOI: 10.1046/j.1365-2389.2003.00533.x.
[27] Furczak J, Joniec J. Polish J Environ Stud. 2009;18:801-810.

LICZEBNOŚĆ I AKTYWNOŚĆ WYBRANYCH GRUP MIKROORGANIZMÓW, CZYNNYCH W PRZEMIANACH WĘGLA W GLEBIE BIELICOWEJ WZBOGACONEJ OSADEM ŚCIEKOWYM

Katedra Mikrobiologii Rolniczej
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Badania laboratoryjne przeprowadzono w dwóch wariantach na glebie bielicowej, do której dodano następujące dawki osadu ścieków komunalno-przemysłowych: 30 Mg · ha^{-1} (1 %), 75 Mg · ha^{-1} (2,5 %), 150 Mg · ha^{-1} (5 %), 300 Mg · ha^{-1} (10 %) i 600 Mg · ha^{-1} (20 %). W jednym wariancie zastosowano osad niesterylny, a w drugim osad poddany procesowi sterylizacji, w celu poznania udziału mikroorganizmów osadowych w transformacji wymienionej materii organicznej Po upływie 0,5, 1, 2, 3, 4 i 5 miesięcy oznaczano w gleby obu wariantów: tzw. ogólną liczbę bakterii o małych wymaganiach pokarmowych, tzw. ogólną liczbę bakterii o dużych wymaganiach pokarmowych, tzw. ogólną liczbę grzybów nitkowatych, liczebność grzybów celulolitycznych, aktywność oddechową, nasilenie procesu mineralizacji celulozy i aktywność dehydrogenaz. Przeprowadzone analizy wykazały, że niesterylny osad ściekowy spowodował zarówno stymulację rozwoju, jak i aktywności badanych grup bakterii i grzybów. Efekt ten na ogół najsilniej wystąpił na początku trwania doświadczenia i nasilał się wraz ze wzrostem dawki odpadu. Osad niesterylny wywarł silniejszy wpływ jedynie na mineralizację celulozy oraz aktywność dehydrogenazową, co może wskazywać na udział w nich drobnoustrojów osadowych.

Słowa kluczowe: gleba, osad sterylny i niesterylny, bakterie, grzyby, oddychanie, mineralizacja celulozy, dehydrogenazy.

DOI: 10.2428/ecea.2012.19(01)002 ECOL CHEM ENG A. 2012;19(1-2):25-33

Bogdan SZOSTAK[1]

CHEMICAL POLLUTION OF SOIL AND WATER ON PIG-BREEDING FARMS

ZANIECZYSZCZENIA CHEMICZNE GLEBY I WODY W OBEJŚCIU FERM TRZODY CHLEWNEJ

Abstract: Farmyards of pig producing farms are a specific source of pollution of the natural environment. In Poland pigs are mainly breed on farms of low animal concentration, which has a minimal negative effect on the environment. The greatest danger for the environment is created by factory pig-breeding farms, whose functioning is particularly troublesome for the residents of the surrounding areas. The places which create the greatest risk for soil contamination are piggeries, areas where natural fertilisers are stored and animal yards. High concentration of animals makes waste management difficult, especially the management of liquid manure. Inappropriate storing of liquid manure and using it as a natural fertilizer may bring about soil devastation and ground and surface water pollution. The following are treated as the chemical indicators of the sanitary condition of soil, specifying its pollution with an organic substance and characterizing the processes of decomposition and mineralization of this substance: the organic nitrogen content and the final products of decomposition of protein substances, that is ammonium and nitrates, organic carbon, and sometimes also some macroelements (P, K, Na, Ca, Mg, S) and microelements (Fe, Mn, Cu, Zn, Mo, Cl, Co).

Keywords: chemical pollution, soil, water, pig, farm

The problem of environment pollution caused by intensive animal breeding is a multi-aspect problem. Hygienic, sanitary and ecological aspects constitute a very important part of this problem, and concern both intensive and extensive pig production.

In recent years, the environment and its impact on human and animal health has been the object of particular interest. One of the conditions of ecological production is keeping the surrounding area clean, that is not exceeding the admissible concentration of harmful substances polluting the air, soil and water. The farmyards of pig farms are sources of contamination of the above enumerated components of the natural environment. The very problem is quite vital since in Poland there are over 600 thousand pig-breeding farms, and the total livestock population of these animals is estimated at about 18 million. In Poland pigs are mainly bred on farms with a low concentration of

---

[1] Department of Animal Breeding and Use, Faculty of Agricultural Science of Zamość, University of Life Science in Lublin, ul. Szczebrzeska 102, 22–400 Zamość, Poland, phone: +48 84 677 27 72, email: bogdan.szostak@up.lublin.pl

animals, which does not have such a negative impact on the environment. The biggest danger for the environment is posed by factory pig-breeding farms, and their functioning is particularly troublesome for residents of the neighbouring areas [1]. Negative ecological effects, such as: natural environment degradation, contamination of soil and rivers and drinking water intakes are among the negative consequences of the excessive concentration of flocks and unfavourable scale of production [2, 3].

Most research conducted so far has been concerned with the influence of animal waste (manure, liquid manure and slurry) on the contamination of arable land. There are not so much detailed research concerning the problem of soil contamination on pig farms, whereas on pig farms and around them there are people and animals, and this contamination may have immediate negative effect on their health and well-being. Farmsteads and their surroundings, as integral parts of farms, are in villages sources of area contamination of an agricultural origin. The areas which are particularly risky as regards soil pollution are piggeries, places where natural fertilizers are stored, and animal yards [3, 4]. Farm animals influence the natural environment directly and indirectly. The natural environment is polluted by dusting and gas pollution of the air, introducing to many organic compounds, mainly nitrogen ones, to soil and water [1, 5], and by microbiological contamination [6–8], including contamination with pathogenic microorganisms. The main source of the natural environment pollution is animal waste, such as manure, liquid manure and slurry [3, 9, 10], which are stored on farms. Very often, inadequate utilization of the existing equipment for manure, liquid manure and slurry management additionally intensifies the degradation of the natural environment in the farmers' residential area and in the surrounding areas, in which food is produced. A high concentration of animals creates problems with waste management, especially slurry management, and its inadequate storing and using as natural fertilizer may cause soil devastation, and ground and surface water pollution [11]. It is understandable that this situation creates some fears for hygienists, sanitary engineers and ecologists, whose concern is protection of human and animal health, production of "healthy" food, and shaping and protection of the environment in village areas [12].

Many authors [13–18] emphasise that the natural environment is more endangered by livestock farm waste than by domestic sewage. In 1980 in Poland the number of substances potentially harmful for the environment included in slurry was 51.3 thousand tons (Mg) of nitrogen and 10.9 thousand tons (Mg) of phosphorus. A ratio between the amount of contamination included in domestic sewage and animal waste for an average community is: 1–41 for nitrogen, 1–37 for phosphorus and 1–60 for potassium [12]. The values given above indicate that the problem of environment pollution caused by the concentration of livestock farms is really big. One of the components of the natural environment which is polluted as a result of unreasonable management of animal waste is soil. A constant contact of people and animals through food and animal feed with soil on which it is produced influences people and animals, their health and productivity. The influence is different depending on the mechanical, physical, chemical and biological properties of soil [19].

A lack of control and inappropriate disposal and neutralization of waste may cause excessive pollution of soil, water and air, which worsens the hygienic conditions and causes a huge epidemiological danger for the surrounding areas. Thus, issues connected with the disposal and neutralization of waste are of primary importance for soil hygiene. In order to maintain its adequate sanitary state, the bacteriological, helmintological and chemical protection is necessary. The sanitary and epidemiological tests are usually carried out together with microbiological, helmintological and chemical tests. Thanks to them it is possible to define the intensity of soil pollution; they can also indicate the source of contamination and approximately define the date when the soil was polluted [13].

The most important chemical indicators of the sanitary condition of soil specifying its contamination with an organic substance and characterising the processes of this substance decomposition and mineralization, are: the content of organic nitrogen and the final products of the decomposition of protein substances, that is ammonia and nitrates, organic carbon, and sometimes also some macroelements (P, K, Na, Ca, Mg, S) and microelements (Fe, Mn, Cu, Zn, Mo, Cl, Co) [13, 20].

Contamination with nitrogen compounds

In agricultural production the main source of nitrogen is animal waste, accumulated, stored and used on most farms as a natural fertilizer in the form of manure, liquid manure and, less commonly, in the form of slurry. Now in Poland the annual production of manure, liquid manure and slurry is about 130 million tons (Mg), which corresponds to the following doses of fertilizer components:

– 35 kg/ha N, which gives 650 thousand tons (Mg) of N a year;
– 9 kg/ha P, which gives 170 thousand tons (Mg) of P a year;
– 35 kg/ha K, which gives 650 thousand tons (Mg) of K a year [5].

The losses of nitrogen during the production of natural fertilizers can be decreased by accumulating all animal waste and storing it better. The state of natural fertilizers management so far significantly restricts the productive functions of natural fertilizers and contributes to the devastation of the environment, especially of the soil environment [3, 5, 11, 12, 16]. Natural fertilisers should be stored in such a way so as to maximally restrict the loss of all the nutritional elements taking place during fermentation [21]. There may be various reasons for losses in manure, liquid manure and slurry. Water may mainly rinse out soluble compounds, such as nitrogen compounds: nitrates, ammonium, amino acids and amides. They are the most valuable compounds, available for plants or quickly becoming available. Therefore, in the water of most wells situated close to dunghills, a harmful content of nitrates has been found: 20–160 mg/dm^3 NO_3^- [22–25]. The protection against the losses caused by rinsing is easy, and the losses may by totally eliminated while storing animal waste such as manure in leakproof spaces or on a layer of absorptive materials, and liquid manure or slurry in leakproof containers securing the inside against water from the outside [5].

When manure is not stored appropriately, the losses of nitrogen may even exceed 50 %, and when it is stored adequately only 10 %, in relation to the initial amount. It means that about 20 kg of nitrogen is saved annually from 1 LU [10, 23]. The possibility to restrict the losses of nitrogen in animal waste management, apart from economic effects (increased cropping), also has a good impact on the environment.

Nitrogen compounds, especially nitrates, which are produced in the process of nitrification, may have a negative impact on the environment. The pollution of water and air takes place when these compounds leave the soil-plant system [5]. Nitrogen in soil is only present in its organic or mineral form, in the amount of 0.1 %. Mineral nitrogen is mainly composed of nitrogen in the ammonium form (NH_4^+) and in the nitrate form (NO_3^-) [20]. The ammonium form of nitrogen gets into soil with rainfall and causes its acidification as a result of nitrification. The processes of nitrification proceed also in manure heaps, and the produced nitrates are either rinsed out or denitrified. As a result of rinsing out nitrates from manure not stored appropriately and from manure water, groundwater and water in village wells become polluted [26]. When there is a lot of ammonium in soil, it means that it is highly contaminated with organic substances of animal origin. With faecal contamination, the number of ammonium ions increases even by ten times. Whereas, if nitrates are present in soil (the final product of the process of nitrification) it means that the process of pollution took place long time ago. In the surface stratum of soil (0–20 cm) close to a piggery, it was found that the amount of mineral, mainly ammonium, nitrogen was about 150 kg N/ha, which corresponds to quite a big amount of nitrogen used in fertilization. The majority of this form of nitrogen resulted from the reduction conditions and the lack of oxygen in the soil which was strongly affected by animal waste [3]. In other tests of soil at different livestock farm objects, the dominant form of nitrogen was nitrate nitrogen in both the surface stratum and deeper strata of the soil profile. The biggest mean amount of nitrate nitrogen was found in soil 10 m from the dunging gutter ($111.52 \text{ mg} \cdot \text{kg}^{-1}$). The content of nitrate nitrogen depended greatly ($P < 0.01$) on the object from which the samples were taken, the soil stratum, and the interaction between the two factors. Ammonium nitrogen showed a tendency to accumulate in the deeper strata of the soil profile. This phenomenon was the most visible at the manure site. In the soil profiles of the yard and around the dunging gutter, a significant increase in the amount of $N\text{-}NH_4^+$ was found, in the 60–80 cm stratum and in the 40–150 cm stratum, respectively. As regards the dunging gutter, the concentration of the analysed component was increasing gradually until it reached the value of $109.68 \text{ mg} \cdot \text{kg}^{-1}$ at the depth of 100–150 cm. The content of ammonium nitrogen in the soil on the analysed farms depended significantly on the object ($P < 0.01$), the depth of the soil profile and the interaction between the factors.

Drinking water contamination is very often connected with the fact that the dunghill is not leakproof, and nitrogen compounds leak into the soil, especially at the manure heaps on the field. Most evidence for nitrogen contamination is provided by water analyses in wells situated close to dunghills or containers for liquid manure. Tests [3] have shown that about 50 % of water in wells on village farms contain over 10 mg $N\text{-}NO_3 \cdot \text{dm}^{-3}$, and 16 % over 40 mg $N\text{-}NO_3 \cdot \text{dm}^{-3}$. The Polish norm is 10 mg $N\text{-}NO_3 \cdot \text{dm}^{-3}$. That is why collecting all the animal waste and storing it in leakproof containers, controlled every year and sealed if necessary, creates a chance for full protection of the soil water environment against nitrate contamination [10].

Contamination with phosphorus compounds

Phosphorus is a chemical element whose excess is also unfavourable and causes degradation of the environment. It is an important, biologically active, component of all living organisms. It is present in soil, natural waters and precipitation. The content of general phosphorus in soil ranges from 0.01 to 0.2 % [20]. In municipal and agricultural sewage, mainly in slurry, the concentration of phosphorus is getting higher and higher. It is connected with the form in which this chemical element is present in animal feed. In grains and in products from processed grains, about 70 % of phosphorus is present in organic connections, mainly in the form of phytic acid and its salts – phytates. Utilisation of phytic phosphorus depends on the presence of phytase enzyme, releasing it from inaccessible organic connections. Phytase is produced by plants, intestinal epithelium of animals and microorganisms existing in the digestive tract. On the whole, the amount of this enzyme is not enough, which significantly restricts the utilization of phytates. Thus, availability of phytic phosphorus is not great, for example in pigs it is about 30 %. Insufficient utilization of phytic phosphorus is a serious ecological problem, because in animal waste there are big amounts of undigested phosphorus. It is estimated that in Poland only cattle and pigs produce annually about 10 thousand tons (Mg) of P_2O_5. The natural environment is endangered in the places where a lot of animal waste is produced, so in the areas with a high concentration of animals [4, 14, 27]. In the tests of soil taken from pig farm areas, 80 kg of dissoluble phosphorus ($P\text{-}PO_4$) per 1 ha [3] were found. The soil at the fattening house and in the yard contained the greatest amounts of phosphorus. This chemical element showed a tendency to accumulate in the deeper strata of soil (100–120 cm), which creates a potential danger for groundwater [4].

Animal waste is utilised as a fertiliser. Plants dynamically absorb phosphorus, maximally up to 1 % of dry matter. The rest of phosphorus, susceptible to soaking, gets into surface and ground waters. Waters are particularly endangered by liquid manure, not only because it flows easily and because of excessive doses of phosphorus, but also because the phosphorus included in it is labile [24]. Pollution of ground and surface waters and open water regions with phosphorus is a serious problem. For example, in Denmark, 8 % of private water intakes do not fulfil the purity standards, and in German as much as 50 %. In Poland it is even worse – in the year of 1987 66 % of household wells provided excessively polluted water. Containers of lentic water are most endangered when there are animal farms in the area. Also sewage pollutes flowing water. It is estimated that about 70 % of the total amount of phosphorus in the Vistula river comes from sewage. The rest gets into waters through rinsing out. Violent rains or thaw contribute to great amounts of phosphorus [27]. That is why special attention must be drawn to the appropriate storing and timely utilization of liquid manure. It is also necessary to appropriately shape the components of the landscape, such as trees, meadows, small water reservoirs, marshland, etc. It will restrict the spread of pollution, cause waste neutralization, and as a result will fasten the regeneration of soil [19].

Other chemical pollution

Greater concentrations of potassium, caused by pollution from animal waste, are present in the surface stratum of soil, whose thickness is about 60 cm, in shallow ground waters and in shallow wells [18]. The total content of potassium in mineral soils in Poland ranges from 0.8–2.1 % [20]. Potassium cation is strongly absorbed both by living organisms and by soil. It can also move together with soaking rainwater into soil water and groundwater. Soil tests soil at different farm objects showed a substantially increased content of potassium in comparison to the reference points, which indicates that animal waste is polluting [3, 4]. Chemical analyses of groundwater from under the enclosure, water from the well and surface water adjacent to the enclosure showed potassium contamination. The presence of high concentration of potassium in groundwater at the level close to, or exceeding, 1000 mg K/m^3 concerns most farms in Poland conducting intensive animal production [3].

Many authors recommend introducing the monitoring of the quality of water and soil from the areas of household enclosures in order to check the content of nitrogen, dissoluble phosphorus and potassium [4, 28].

Sulfate sulphur is an indicator of the anthropogenic pollution of soil. Estimation of the content of sulphur in soil is necessary due to its influence both on the mobility of heavy metals and on the worsening of the chemical properties of soil, and above all on activating aluminium and losses of magnesium. These phenomena create serious ecological dangers [20].

The author's research [29] concerning the content of general sulphur and sulphate sulphur in the soil from pig farms did not found its high concentrations. The highest content of general sulphur was found in the surface stratum of soil (0–20 cm) on the sow yard ($68.42 \text{ mg} \cdot 100 \text{ g}^{-1}$) and at the fattening house ($53.08 \text{ mg} \cdot 100 \text{ g}^{-1}$). Also the soil from the sow yard contained the greatest amounts of sulphate sulphur ($12.83 \text{ mg} \cdot 100 \text{ g}^{-1}$). The phenomenon of accumulating sulphur at the depth of 40–69 cm was observed. In one of the analysed farms, about 42 % of samples were characterized by the 4th grade of sulphate sulphur content in soil.

Heavy metals are found not only in the highly industrialised regions, but also in natural ecosystems, used agriculturally. The harmfulness of heavy metals results from their biological and biochemical properties. One such property is the susceptibility to bioaccumulation from the soil environment [13, 25]. The soil from farmyards may be the source of animal contamination with heavy metals, especially in the farmyards situated close to public roads [30]. Heavy metals are introduced into the agricultural ecosystem (soil and water) through rainfall and animal waste. Pig waste, both liquid and solid, may contain heavy metals such as: Pb, Zn, Cu, Ni, Cr and others [31].

The author's own research [32] concerning the content of selected heavy metals (Pb, Zn and Mn) in soil at various farm objects found that permissible norms for the chemical elements tested had not been exceeded. It was noted that there was a difference in the content of heavy metals, depending on where the samples had been taken. The highest values of the analysed elements were found in the soil from the animal yard. The results of our research [4, 29, 32] confirm Pawlak's statement [33] that keeping pigs in yards was connected with increasing the risk of chemical pollution and microbiological pollution of soil and water, as compared with keeping animals in closed spaces.

Summary and recommendations

So far, the ecological danger connected with pig production in Poland has not been big thanks to the small sizes of the farms. However, recently, the concentration of production may be observed, which poses more danger for the natural environment. The impact of pig production on the natural environment concerns all its elements: water, soil and air. Thus, it is important that the quality of water and soil from farm enclosures be inspected with regard to the nitrogen, dissoluble phosphorus and potassium content.

A pig farm and its surrounding area in village areas is the source of area pollution of agricultural origin. The areas which are most dangerous are: piggeries, animal yards, dunging gutters and manure and liquid manure containers. Farm objects for storing animal waste, depending on their kind, technical condition and capacity, create the greatest risk for soil and water pollution with nitrogen, phosphorus and potassium compounds.

In order to prevent losses of fertiliser components and to protect the environment against pollution, animal waste should be stored appropriately and used rationally in agriculture.

It is important to undertake some action to decrease the danger for the natural environment by increasing supervision to make sure that in the farms with high concentration of animals technological regimes are abided by, as well as the requirements enforced by the Code of Good Agricultural Practice. Education is an effective method to improve the soil and water quality on a farm. That is why farmers and agricultural services workers should be trained continuously on the modern systems of animal breeding to limit its negative impact on the environment.

References

[1] Szymańska E. Wpływ chowu trzody chlewnej na środowisko. Zesz Nauk AR Wrocław. 2006;540:531-536.
[2] Delgado ChL. Policy, technical and environmental determinants and implications of the scaling-up of livestock production in four fast-groving developing countries: A synthesis. FAO, Washington:2004.
[3] Sapek B, Sapek A. Nawozy naturalne w zagrodzie wiejskiej i jej otoczeniu a jakość wody i gleby na tym terenie. Wieś Jutra. 2008;3:24-27.
[4] Bekier-Jaworska E, Szostak B. Wpływ ferm trzody chlewnej na zawartość pierwiastków biogennych w glebie. Acta Agrophys. 2003;I(4):607-615.
[5] Kuszelewski L. Racjonalna gospodarka odchodami zwierzęcymi pod kątem ograniczania strat azotu. Zesz. Edukacyjne IMUZ Falenty. 1997;2:17-29.
[6] Czernomys-Furowicz D, Furowicz A. Bakterie patogenne w glebie – zagrożenia epizootiologiczne i epidemiologiczne. Przeg Hodowl. 1996;3:26-30.
[7] Cools D, Merckx R, Vlassak K, Verhaegen J. Survival of E coli and Enterococcus spp. derived from pig slurry in soils of different texture. Appl Soil Ecol. 2001;17(1):53-62.
[8] Jezierska-Tys S. Badania nad skażeniem mikrobiologicznym i chemicznym gnojowicy bydlęcej i trzody chlewnej. Ann UMCS Lublin. 1987;XLII:261-269.
[9] Kutera J, Hus S. Rolnicze oczyszczanie i wykorzystanie ścieków i gnojowicy. Wyd AR Wrocław; 1998.
[10] Sapek A, Sapek B, Pietrzak S. Zagęszczenie produkcji rolnej w zagrodzie jako źródło zanieczyszczenia wody. Zesz Probl Post Nauk Roln. 1998;459:103-124.

[11] Gołaś Z, Kozera M. Ekologiczne konsekwencje koncentracji produkcji trzody chlewnej. J Agribus Rural Develop. 2008;1(7):29-42.
[12] Rossa L.: Wstępna ocena wpływu odchodów zwierzęcych na środowisko gruntowo-wodne na przykładzie Zakładu Doświadczalnego IMUZ w Falentach. Wiad Melior Łąkar. 1998;1(41):37-40.
[13] Giercuszkiewicz-Bajtlik M. Ocena wpływu na środowisko wodne obiektów rolniczego wykorzystania ścieków i gnojowicy oraz inwestycji związanych z hodowlą zwierząt. Poradnik Inst Ochr Środow. Warszawa: 1998.
[14] Jamroz D. Zmniejszenie obciążenia środowiska przez modyfikację żywienia zwierząt użytkowych. Materiały Konf Nauk.-Techn. Pasze a ochrona środowiska, Puławy; 1997:19-32.
[15] Kluczek JP. Problemy mikrobiologicznego skażenia gleby. Pr Kom Nauk Roln Biol. BTN Bydgoszcz: 1995;B43(31):5-27.
[16] Kutera J. Zagospodarowanie nawozów naturalnych zgodnie z ustawą o nawozach i nawożeniu z uwzględnieniem ochrony środowiska. Zesz Probl Post Nauk Roln. 2001;475:319-326.
[17] Roszkowski A. Intensywna produkcja zwierzęca a Kodeks Dobrych Praktyk Rolniczych. Materiały z IV Międzynarodowej Konferencji Naukowej “Problemy intensyfikacji produkcji zwierzęcej przy uwzględnieniu ograniczeń ochrony środowiska”, Warszawa; 1998:186-193.
[18] Sapek B, Urbaniak M. Ocena zanieczyszczeń gleby z terenu zagrody i jej otoczenia składnikami nawozowymi w gospodarstwach demonstracyjnych projektu BAAP II. Wiad Melior Łąkar. 2001;1:32-36.
[19] Tymczyna L, Chmielowiec-Korzeniowska A. Higiena środowiska wiejskiego. Wyd. AR. Lublin: 2002.
[20] Baran S. Ocena stanu degradacji i rekultywacji gleb. Wyd AR. Lublin: 2000.
[21] Ustawa o nawozach i nawożeniu DzU Nr 89, poz. 991.
[22] Kutera J. Preferowane technologie gospodarki gnojówką i gnojowicą w Polsce. Post. Nauk Roln. 1999;1:95-103.
[23] Marcinkowski T. Bilans azotu oraz zawartość azotanów w środowisku glebowo-wodnym w gospodarstwach rolnych regionu Żuław Wiślanych. Zesz Probl Post Nauk Roln. 1996;440:231-237.
[24] Mazur T, Sądej W. Wymywanie składników pokarmowych z gleby nawożonej gnojowicą trzody chlewnej, obornikiem i nawozami mineralnymi. Fol Univ Agric Stetin 200 Agricult Ann. 1999;77:25-262.
[25] Oudendag DA, Leusink HH. The Manure Model: manure, minerals (N, P and K) ammonia emission, heavy metals and the use of fertilizer in Dutch agriculture. Environ Pollut. 1998;102(SI):241-246.
[26] Mazur T. Zagadnienia nawożenia i ochrony środowiska. Wykład inauguracyjny, UW Wrocław: 2002.
[27] Zdunek B. Fosfor – jeden z czynników zagrożenia ekologicznego. Przegl Hodowl. 1995;4:17-18.
[28] Romaniuk W, Domasiewicz T, Karbowy A, Wardal WJ. Ograniczenie wpływu produkcji zwierzęcej na środowisko. Inżyn Roln. 2009;1(110):233-242.
[29] Szostak B, Bekier-Jaworska E. Content of total sulphur and sulphate sulphur in the soil on pig farms. Ecol Chem Eng. 2005;12(11):1289-1293.
[30] Bojarczyk W, Kwiecień M. Drogi przenikania ołowiu i kadmu do organizmu zwierząt. Przegl Hodowl. 2000;12:22-24.
[31] Mihułka M, Chuto J, Wrońska D, Nowakowska A, Perłakowska M. Charakterystyka technologiczna hodowli drobiu i świń w Unii Europejskiej. Ministerstwo Środowiska, Warszawa: 2003.
[32] Szostak B. Content of selected heavy metals in soil in various areas of the swine farm. Ecol Chem Eng A. 2009;16(1–2):77-81.
[33] Pawlak J. Technologia produkcji zwierzęcej a środowisko naturalne. Probl Inż Roln. 2008;4:5-91.

ZANIECZYSZCZENIA CHEMICZNE GLEBY I WODY W OBEJŚCIU FERM TRZODY CHLEWNEJ

Wydział Nauk Rolniczych w Zamościu
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Obejścia gospodarstw nastawionych na produkcję świń są swojego rodzaju źródłami zanieczyszczenia środowiska naturalnego. W Polsce dominuje chów trzody chlewnej w gospodarstwach o niskiej koncentracji zwierząt, który w minimalnym stopniu ujemnie wpływa na środowisko. Największe zagrożenie dla środowiska stanowią wielkoprzemysłowe fermy świń, których funkcjonowanie jest szczególnie uciążliwe dla mieszkańców okolicznych terenów. Miejscami stwarzającymi największe ryzyko zanieczyszczenia gleby w są chlewnie, miejsca składowania nawozów naturalnych, okólniki dla zwierząt. Duża koncentracja zwierząt stwarza trudności z zagospodarowaniem odpadów, zwłaszcza gnojowicy, a niewłaściwe jej przechowywanie i stosowanie jako nawozu naturalnego może powodować dewastację gleby, zanieczyszczenie wód powierzchniowych i podziemnych. Za najważniejsze wskaźniki chemiczne stanu sanitarnego gleby, określające zanieczyszczenie jej substancją organiczną i charakteryzujące procesy rozkładu i mineralizacji tej substancji przyjmuje się: zawartość azotu organicznego oraz końcowych produktów rozkładu substancji białkowych, tj. amoniaku i azotanów, a także węgla organicznego, a niekiedy również niektórych makro- (P, K, Na, Ca, Mg, S) i mikroelementów (Fe, Mn, Cu, Zn, Mo, Cl, Co).

Słowa kluczowe: zanieczyszczenia chemiczne, gleba, woda, świnie, ferma

DOI: 10.2428/ecea.2012.19(01)003 ECOL CHEM ENG A. 2012;19(1-2):35-43

Jean B. DIATTA[1]

APPLICATION OF GEOCHEMICAL INDICES FOR ASSESSING LEAD AND CADMIUM CONTAMINATION IN RECREATIONAL PARKS OF THE CITY POZNAN

ZASTOSOWANIE WSKAŹNIKÓW GEOCHEMICZNYCH DO OCENY ZANIECZYSZCZENIA OŁOWIEM i KADMEM W REKREACYJNYCH PARKACH POZNANIA

Abstract: Recreational Parks (RP) of the city Poznan were investigated in October 2009 in order to evaluate contamination state of their soils by lead and cadmium. From the Recreational Park Marcinkowski – RPM, Recreational Park Solacki – RPS, Recreational Park Wodziczko – RPW and Recreational Park Piatkowo – RPP the soil samples were collected at two depths, ie 0–10 and 10–20 cm, in the quantity of 36, 52, 32 and 34, respectively. The total content of Pb and Cd was determined in these samples, as well as some their selected physical and chemical properties. Detailed assessment of the soil contamination state was undertaken on the basis of different indices such as geochemical accumulation index (I_{geo}), factor (C^i_f) and degree (C_{deg}) of contamination.

The evaluation of soils made by applying Pb-I_{geo} has shown that parks may be ranged as follows: RP Piatkowo < RP Solacki < RP Wodziczko < RP Marcinkowski. The concern and threat related to the impact of Pb on humans requires more restrictive limits of content, hence geochemical background (GB) values as reported by Czarnowska [20] may be considered as more adapted for protecting from potential health hazards. In the case of cadmium, the Cd-I_{geo} based contamination assessment allowed to organize parks accordingly: RP Piatkowo < RP Marcinkowski < RP Solacki < RP Wodziczko. Cadmium contribution in the overall contamination (C_{deg}) changed as did the Cd-I_{geo} indices. This was mostly reflected in the RPs Wodziczko and Solacki and intermediately in the RP Marcinkowski. On the basis of the performed geochemical evaluation of soil Recreational Park Piatkowo is the sole to be classified as free from Pb and Cd contamination threat.

Keywords: recreational parks, Poznan, Pb, Cd, soil, geochemical indices, contamination factor and degree

As a number of people living in towns and cites has increased, larger human populations are being exposed to the negative effects of the urban environment. Sources of pollution vary according to specific industrial, geographical, geological, climatic and sociological conditions, but in all cases road traffic is one of the most important ones and it influences all parts of the environments [1, 2]. The chemistry of pollutants,

---

[1] Department of Agrochemistry and Environmental Biogeochemistry, University of Life Sciences in Poznan, ul. Wojska Polskiego 71F, 60–625 Poznań, Poland, phone: +48 61 848 77 83, email: Jeandiatta63@yahoo.com

including metals, in urban soils is far from understood, and several aspects of the dynamics of metals pollutants in urban soils need further study. In the last few years, soils in many cities have been studied [3–11].

In pollution research soil is mainly considered as a medium of plant growth and agriculture production but in urban conditions, changes in the chemical nature of the soil may lead to adverse interactions with building materials, toxicity to soil flora and fauna and influence exposure of the population particularly young children, to toxic substances. Among the various toxic elements in the urban environment, lead and cadmium are considered to be the most hazardous. In the case of lead, its harmful effects are still debated, some reports have presented evidence of its neurotoxicity, especially for children [12–15].

Pollution of soil by potentially toxic metals is often assessed on the basis of total metal concentrations. However, many forms of metals are strongly held in soils and generally become immobile, although several factors (changes in pH or redox conditions, soluble organic complexing agents, etc) may mobilize such forms [16–18]. Several approaches have been used for evaluating the degree of heavy metals contamination in different ecosystems. They are commonly based on the amounts of metals extracted by applying specified soil tests or on the elaboration of phytotests, which are expected to confirm or not metal concentrations extracted by soil tests [19–22]. Indices-based assessment of soils contamination by heavy metals seems to be a useful geochemical method, since they simplify and reorganize quantitative data into unitless parameters [10, 23–25].

Therefore, the current work is intended to focus on indices, such as the index of geoaccumulation (I_{geo}), contamination factor (C_f) and degree of contamination (C_{deg}) for evaluating the potential contamination by Pb and Cd of soils of selected Recreational Parks of the city Poznan.

Materials and methods

Soil samples were collected at two depths, 0–10 and 10–20 cm, in October 2009 at four Recreational Parks (RP) within the city Poznan. This sampling procedure was adopted in order to outline the possible effect of maintenance practices (lawn and paths establishment) on metal levels. These are Recreational Park Marcinkowski – RPM (36 samples), Recreational Park Solacki – RPS (52 samples), Recreational Park Wodziczko – RPW (32 samples) and Recreational Park Piatkowo – RPP (34 samples). Details about physical and chemical analyses of soil materials are reported in the paper *Assessment of heavy metals contamination of selected Recreational Parks of the city Poznan*, this issue (Ecol. Chem. Eng. A 2011, 18(9–10), 1211–1217). Total contents of lead (Pb), and cadmium (Cd), (mean of 0–10 and 10–20 cm), were assayed by hot-digestion in *aqua regia* chemical test [26]. The indices-based assessment of the soils contamination state of these sites was undertaken throughout applying reference data [19, 20]. Specific developments are listed as under:

a) Index of geoaccumulation (I_{geo}). This index enables the assessment of heavy metal contamination by comparing current and preindustrial metal contents. It was originally used for bottom sediments [23], but may be applied for assessing soil contamination on the basis of the following equation:

$$I_{geo} = \log_{10} \frac{C_n}{1.5\, B_n} \tag{1}$$

where: C_n – the concentration of the element n in the pelitic sediment fraction (< 2 μm),
B_n – the geochemical background value in the fossil argillaceous sediment (ie, average shale),
1.5 – the constant allows for involving natural fluctuations in the concentration of a given substance in the environment and very small anthropogenic influences.

Seven classes of soil quality were suggested by Muller [23] on the basis of index of geoaccumulation value (Table 1).

Table 1

Classes of soil quality on the basis of index of geoaccumulation value [23]

Class	Value	Soil quality
0	$I_{geo} \le 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated
4	$3 < I_{geo} < 4$	Heavily contaminated
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

A modified method was applied in the current paper for the computations of the I_{geo} values and deals with the following details: C_n expresses the total content (mean values) of a given metal in the surface layer (ie 0–10 and 10–20 cm) of the tested soils, while B_n, the content of the same metal expressed as the *Background Level for Poland* (BLP) [19] and *Geochemical Background* (GB) [20]. These values are reported in Table 5.

b) Contamination factor (C^i_f) and degree of contamination (C_{deg}). Soil contamination was also evaluated by using indices such as the contamination factor (C^i_f) and the degree of contamination (C_{deg}) [24], which were computed on the basis of the below equation:

$$C^i_f = \frac{C^i_{0-1}}{C^i_n} \tag{2}$$

where: C^i_{0-1} – the mean content of metals from at least five sampling sites,
C^i_n – the preindustrial content of individual metals.

A modification was done and consisted of using the content of metals expressed as the Background Level for Poland (BLP) [19] and Geochemical Background (GB) [20]. Four categories have been suggested by Hakanson [24] (Table 2).

Table 2

Categories of contamination factor on the basis of C_f^i value [24]

Contamination factor	Description
$C_f^i < 1$	Low contamination factor
$1 \le C_f^i < 3$	Moderate contamination factor
$3 \le C_f^i < 6$	Considerable contamination factor
$6 \le C_f^i$	Very high contamination factor

Moreover it should be mentioned that C_f^i is a single-element index. The sum of C_f^i for all studied metals yields the so-called contamination degree (C_{deg}) of the ecosystem and is represented by four classes (Table 3).

Table 3

The contamination degree (C_{deg}) of the ecosystem

Contamination degree	Description
$C_{deg} < 8$	Low degree of contamination
$8 \le C_{deg} < 16$	Moderate degree of contamination
$16 \le C_{deg} < 32$	Considerable degree of contamination
$32 \le C_{deg}$	Very high degree of contamination

Computations were made by using the Excel® Sheet and simple statistical analysis by the Statgraphics Software facilities.

Results and discussion

The occurrence of lead and cadmium in elevated concentrations or in excess in the environment is being widely reported due to the harmful effects of these metals. In fact the determined amounts do not uniformly give a common consent in terms of direct or indirect awareness. The application of geochemical indices for classifying significantly disparate sites may be treated as a useful tool in this matter.

Data listed in Table 4 decidedly show the great heterogeneity in Pb and Cd contents (with standard deviation – SD values) in soils of Recreational Parks. These amounts as compared with the Background Levels for Poland (Pb_{BLP}) revealed that only the RP Marcinkowski may be considered as moderately contaminated by Pb, whereas when referred to the Geochemical Background (Pb_{GB}), the contamination state shifted even into very severe contamination/ pollution (case of RPs Marcinkowski, Solacki and Wodziczki). Cadmium contents appeared to be of great concern, since all were decidedly beyond both Cd_{BLP} and Cd_{GB}. Therefore, the application of geochemical-

-based indices for evaluating Pb and Cd contamination state of these parks may provide targeted information, whether we are facing a threat or a slight contamination.

Table 4

Total heavy metal content of soils within investigated Recreational Parks of the city Poznan (mean of 0–10 and 10–20 cm)

Metal	*RPM* ($n = 36$)[a]	*RPS* ($n = 52$)[b]	*RPW* ($n = 32$)[c]	*RPP* ($n = 34$)[d]
	[mg · kg^{-1}]			
Pb	[α]56.4 ± 25.0[β]	32.0 ± 20.6	40.1 ± 18.2	13.0 ± 15.3
Cd	1.58 ± 0.42	2.12 ± 1.57	2.42 ± 1.58	0.87 ± 1.20
Reference values [mg · kg^{-1}]				
Background Level for Poland[x]	Pb_{BLP}	40.0	Cd_{BLP}	0.65
Geochemical Background[y]	Pb_{GB}	9.8	Cd_{GB}	0.18

Recreational Parks: [a] – Marcinkowski, [b] – Solacki, [c] – Wodziczko, [d] – Piatkowo; [α] – Mean value; [β] – Standard Deviation; [x] – acc. to Kabata-Pendias et al [19]; [y] – acc. to Czarnowska [20].

Lead

Lead geoaccumulation indices (Pb-I_{geo}) indicated a contamination state, whose magnitude depended on the BLP and GB values exhibiting Pb-I_{geo} indices in the ranges from –0.85 to –0.08 and –0.24 to 0.53, respectively (Table 5).

Table 5

Geochemical indice (I_{geo}) values calculated for the investigated parks

Parameter	Metal	Recreational Park			
		Marcinkowski	Wodziczki	Solacki	Piatkowo
I_{geo}	Pb_{BLP}*	–0.08	–0.23	–0.36	–0.85
	Pb_{GB}	0.53	0.39	0.25	–0.24
	Cd_{BLP}	0.20	0.31	0.22	–0.23
	Cd_{GB}	0.75	0.87	0.77	0.33

* Explanations see Table 4.

These ranges fit the contamination class [23] extending mostly from < 0 to 1 and may be designated as practically uncontaminated in the case of BLP based Pb-I_{geo} to moderately contaminated for the GB. On the basis of these indices the contamination level of soils within parks follows the order, ie from the less contaminated up to the most: RP Piatkowo < RP Solacki < RP Wodziczko < RP Marcinkowski.

A specific evaluation of the overall contamination level was carried out throughout the degree of contamination (C_{deg}), (Table 6). Furthermore, a detailed estimation was undertaken by using contamination factors (C_f^i), which mean values allowed to classify [24] soils moderate contamination factor accordingly to BLP and GB values.

Table 6

Contamination factors and degrees for particular Pb of the investigated Recreational Parks for BLP and GB values*

Recreational park	Contamination factor (Range)			Mean	Share [%] of C_f^i to C_{deg}
Marcinkowski	Pb_{BLP}	C_f^i	0.96–2.63	1.41 ± 0.63	40
	Pb_{GB}		1.46–10.74	5.75 ± 2.55	
Wodziczko	Pb_{BLP}		0.31–2.17	1.00 ± 0.47	28
	Pb_{GB}		1.58–8.86	4.09 ± 1.94	
Solacki	Pb_{BLP}		0.10–2.47	0.80 ± 0.51	23
	Pb_{GB}		0.42–10.07	3.26 ± 2.10	
Piatkowo	Pb_{BLP}		0.05–2.34	0.33 ± 0.41	9
	Pb_{GB}		0.20–9.53	1.33 ± 1.69	
Degree of contamination (BPL) $\left[C_{deg} = \sum(C_f^{\text{Pb, Cd}})\right]$			1.42–11.03	3.54 ± 2.02	—
Degree of contamination (GB)			3.66–39.20	14.43 ± 8.28	

* Explanations see Table 4.

Three classes were operationally established, relatively to both values:

– Pb_{BLP}: only RP Marcinkowski exhibited a moderate contamination factor,

– Pb_{GB}: all parks represented a considerable contamination factor, except the RP *Piatkowo*, characterised by moderate contamination factor.

Importantly it should be observed, that the mean C_{deg}-based BLP and GB reference values varied from 3.54 to 14.43, respectively, describing decidedly a low degree ($C_{deg} < 8$) and moderate degree of contamination ($8 < C_{deg} < 16$) as suggested by Hakanson [24]. The overall share of Pb in the level of contamination of investigated parks decreased similarly to the Pb-I_{geo} indices. The impact of Pb in the bulk contamination was ca 26 % for the RP Solacki and Wodziczki, but raised up to 40 % in the case of the RP Marcinkowski. The last one is located in the city centre, hence reflected the direct anthropogenic origin of Pb. The re-evaluation of the degree of contamination revealed that the application of both reference values was found useful for such specific sites like city Recreational Parks. The concern and threat related to the impact of Pb to humans requires more restrictive limits, hence geochemical background (GB) values as reported by Czarnowska [20] may be considered as more adapted for protecting from potential health hazards [12, 14, 15, 17].

Cadmium

Indices of Cd geoaccumulation (Cd-I_{geo}) indicated general ranges varying from –0.23 to 0.87 of which the Cd-I_{geo} based BLP and RV values fluctuated accordingly: –0.23 to 0.31 and 0.33 to 0.87 (Table 2). Contamination assessment based on these indices may create some discrepancies related to the establishment of a proper Cd-I_{geo} class. Therefore, it could be reasonable to group both classes into one with a range varying from 0.20 to 0.87, ie, uncontaminated to moderately contaminated [23]. This outlines the cadmium contamination status, which seems to be of great concern, irrespective of the investigated parks and ranged in decreasing order as follows: RP Piatkowo < RP Marcinkowski < RP Solacki < RP Wodziczko. Interestingly, it may be observed, that this order is divergent from that established for Pb-I_{geo}.

Data listed in Table 4 deal with values of contamination factors (C_f^i) [24] and those related to the overall contamination degree (C_{deg}) accordingly to the reference values BLP and GB. The ecological specificity of cadmium resides in its enhanced mobility [27] and hence its contamination is easily disseminated in the environment. The RPs Solacki and Wodziczko undergo frequent and intensive maintenance activities involving among others the incorporation of compost-like materials for improving grasses and shrubs growth conditions. This may explain the position they occupy in these ranges in the case of cadmium. Changes observed in the case of the C_f^i indices reflect the contamination state, which varied proportionally with reference values. Then for the BLP [19], C_f^i values fluctuated within the range 1.34–3.72 implying the occurrence of a moderate to considerable contamination factor, whereas for the GB [20] based C_f^i evaluation, quite all indices (except the RP Piatkowo) exceeded the threshold, ie $6 < C_f^i$, indicative of a very high contamination factor. This concerns particularly the RPs Wodziczko and Solacki characterised by C_f^i amounting to 13.43 and 11.78, respectively, followed by the RP Marcinkowski, ie $C_f^i = 8.78$.

The overall contamination degree (C_{deg}) as suggested by Hakanson [24] exhibited significantly high (C_{deg}-based BLP) and exceptionally very high (C_{deg}-based GB) indices, amounting accordingly 10.75 and 38.82 (Table 7). The latter ones fitted the ranges $8 < C_{deg} < 16$ designated as moderate degree of contamination and $32 < C_{deg}$, ie very high degree of contamination.

Table 7

Contamination factors and degrees for particular Cd of the investigated Recreational Parks for BLP and GB values*

Recreational park	Contamination factor (Range)			Mean	Share [%] of C_f^i to C_{deg}
Marcinkowski	$\mathrm{Cd}_{\mathrm{BLP}}$	C_f^i	1.31–4.29	2.43 ± 0.65	23
	Cd_{GB}		4.72–15.50	8.78 ± 2.36	
Wodziczko	$\mathrm{Cd}_{\mathrm{BLP}}$		0.91–10.25	3.72 ± 2.49	35
	Cd_{GB}		3.28–37.00	13.43 ± 8.99	
Solacki	$\mathrm{Cd}_{\mathrm{BLP}}$		0.57–9.48	3.26 ± 2.54	30
	Cd_{GB}		2.06–34.22	11.78 ± 9.18	
Piatkowo	$\mathrm{Cd}_{\mathrm{BLP}}$		0.32–11.02	1.34 ± 1.95	12
	Cd_{GB}		1.14–39.78	4.83 ± 7.04	
Degree of contamination (BPL) $\left[C_{deg} = \sum(C_f^{\mathrm{Pb,\,Cd}})\right]$			3.11–35.04	10.75 ± 7.63	—
Degree of contamination (GB)			11.20–126.35	38.82 ± 27.57	

* Explanations see Table 4.

Cadmium contribution in the overall contamination changed as did the Cd_{Igeo} indices. This was mostly reflected in the RPs Wodziczko and Solacki and intermediately in the RP Marcinkowski. Less concern related to Cd contamination may be observed in the case of the RP Piatkowo, where Cd and Pb direct contribution in the overall contamination share was quite similar. On the basis of the performed geochemical evaluation this park is the sole to be classified as free from any contamination threat.

Conclusions and statements

The assessment of the state of Poznan Recreational Parks contamination of soils by lead and cadmium undertaken by applying geochemical indices (I_{geo}, C_f^i and C_{deg}) has revealed the impact of anthropogenic pressure on these ecosystems. Data have shown, that on the basis of Pb based I_{geo} indices the contamination level of soils within parks follows: RP Piatkowo < RP Solacki < RP Wodziczko < RP Marcinkowski. Moreover it was suggested that the concern and threat related to the impact of Pb on humans requires more restrictive limits, hence geochemical background (GB) values as reported by Czarnowska [20] may be considered as more adapted for protecting from potential health hazards.

The cadmium contamination status of soils appears to be of great concern, irrespective of the investigated parks and represented the order: RP Piatkowo < RP Marcinkowski < RP Solacki < RP Wodziczko. Cadmium contribution in the overall contamination (C_{deg}) changed as did the Cd_{Igeo} indices. This was mostly reflected in the RPs Wodziczko and Solacki and intermediately in the RP Marcinkowski. On the basis of the performed geochemical evaluation Recreational Park Piatkowo soil is the sole to be classified as free from any contamination threat.

Acknowledgement

Authors acknowledge the funding support of investigations within the project of the city Poznań: Proj.bad.M.P-ń um.RoM.V/3420, 2009.

References

[1] De Kimpe RR, Morel JL. Soil Sci. 2000;165:31-40.
[2] Greinert A. Ochrona i rekultywacja terenów zurbanizowanych. Wyd. Politechniki Zielonogórskiej; 2000, Monografia nr 97, ISBN 83-85911-12-X.
[3] Mielke HW. Environ Geochem Hlth. 1994;16(3/4):123-128.
[4] Beyer L, Cordsen E, Blume HP, Schleuss U, Vogt B, Wu Q. Soil Technol. 1996;9:121-132.
[5] Paterson E, Sanka M, Clark L. Appl Geochem. 1996;11:129-131.
[6] De Miguel E, Jimenez de Grado M, Llamas JF, Martin-Dorado A, Mazadiego LF. Sci Total Environ. 1998;215:113-122.
[7] Chronopoulos J, Haidouti C, Chonopoulou-Sereli A, Massas I. Sci Total Environ. 1997;196:91-98.
[8] Sanchez Martin MJ, Sanchez Camazano M, Lorenzo LF. B Environ Contam Tox. 2000;64:250-257.
[9] Birke M, Rauch U. Environ Geochem Hlth. 2000;22:233-248.
[10] Diatta JB, Grzebisz W, Apolinarska K. EJPAU; 2003:6(2) [online]. http://www.ejpau.media.pl/articles/volume6/issue2/environment/art-01.pdf
[11] Madrid L, Diaz-Barrientos E, Reinoso R, Madrid R. Eur J Soil Sci. 2004;55:209-217.

[12] Sheppard SC, Evenden WG, Schwartz WJ. J Environ Qual. 1995;24:498-505.
[13] Turkdogan MK, Kilicel F, Kara K, Tuncer I. Environ Toxicol Phar. 2002;13:175-179.
[14] Kulka E. Ocena ekspozycji dzieci uczęszczających do przedszkól na ołów i kadm. Wieloletni program – Środowisko i Zdrowie. Instytut Ekologii Terenów Uprzemysłowionych. 2004;6:6-8.
[15] Kondej D. Bezpieczeństwo Pracy. 2007;2:25-27.
[16] McBride MB. Adv Soil Sci. 1989;10:1-56.
[17] Gupta SK., Vollmer M.K. and Krebs R.: Sci. Total Environ. 1996;178:11-20.
[18] Diatta JB. Pol J Environ Stud. 2006 ;15(2):219-227.
[19] Kabata-Pendias A, Piotrowska M, Motowicka-Terelak T, Maliszewska-Kordybach B, Filipiak K, Krakowiak A, Pietruch C. Podstawy oceny chemicznego zanieczyszczenia gleb. Metale ciężkie, siarka i WWA. Biblioteka Monitoringu Środowiska, PIOŚ, Warszawa: IUNG; 1995.
[20] Czarnowska K. Roczn Glebozn. 1996;XLVII(supl.):43-50.
[21] Reimann C, Siewers U, Tarvainen T, Bityukova L, Eriksson J, Gilucis A. Sci Total Environ. 2000;257:155-170.
[22] Yang JK, Barnett MO, Jardine PM, Brooks SC. Soil Sediment Contam. 2003;12(2):165-179.
[23] Müller G. Geojournal. 1969;2:08-118.
[24] Hakanson L. Water Res. 1980;14:975-1001.
[25] Saňka M, Strnad M, Vondra J, Paterson E. Int J Environ Anal Chem. 1994;59:327-343.
[26] International Standard: Soil Quality - Extraction of trace elements soluble in aqua regia. ISO 11466, Geneva 1995.
[27] Nouri J, Alloway BJ, Peterson PJ. Pakistan J Biol Sci. 2001;4(10):1285-1287.

ZASTOSOWANIE WSKAŹNIKÓW GEOCHEMICZNYCH DO OCENY ZANIECZYSZCZENIA OŁOWIEM i KADMEM W REKREACYJNYCH PARKACH POZNANIA

Katedra Chemii Rolnej i Biogeochemii Środowiska
Uniwersytet Przyrodniczy w Poznaniu

Abstrakt: Rekreacyjne Parki (RP) miasta Poznań zbadano w październiku 2009 r. w celu oceny stanu zanieczyszczenia ich gleb ołowiem i kadmem. Z Parku Marcinkowskiego – RPM, Parku Sołackiego – RPS, Parku Wodziczki – RPW i Parku Piątkowo – RPP pobrano próbki gleby z dwóch głębokości (0–10 i 10–20 cm) w ilości odpowiednio: 36, 32, 52 i 34. Oznaczono całkowitą zawartość Pb i Cd oraz wybrane właściwości fizyczne i chemiczne tych próbek gleby. Szczegółową ocenę stanu zanieczyszczenia gleb przeprowadzono na podstawie różnych wskaźników, takich jak: geochemiczny indeks akumulacji (I_{geo}) oraz współczynnik (C^i_f) i stopień (C_{deg}) zanieczyszczenia.

Ocena gleb na podstawie I_{geo} wykazała, że w przypadku Pb parki można uszeregować następująco: RP Piątkowo < RP Sołacki < RP Wodziczki < RP Marcinkowskiego. Z uwagi na negatywne oddziaływanie Pb na ludzi, progi jego zawartości powinny być bardziej restrykcyjne, stąd należałoby rozważyć zastosowanie wartości tła geochemicznego (GB) wg Czarnowskiej [20] jako bardziej odpowiedniego dla ochrony przed potencjalnym zagrożeniem zdrowia. Na podstawie stanu zanieczyszczenia gleb kadmem (Cd-I_{geo}) badane parki można uszeregować następująco: RP Piątkowo < RP Marcinkowskiego < RP Sołacki < RP Wodziczki. Udział Cd w ogólnym zanieczyszczeniu gleb (C_{deg}) kształtował się zgodnie z wartościami wskaźników Cd-I_{geo}. Najwyraźniej zaznaczyło się to w RP Wodziczko i Sołacki oraz pośrednio w RP Marcinkowski. Na podstawie wykonanej oceny geochemicznej gleb jedynie Rekreacyjny Park Piątkowo można sklasyfikować jako wolny od zagrożenia zanieczyszczeniem ołowiem i kadmem.

Słowa kluczowe: parki rekreacyjne, Poznań, Pb, Cd, gleba, wskaźniki geochemiczne, indeks i stopień zanieczyszczenia

DOI: 10.2428/ecea.2012.19(01)004 ECOL CHEM ENG A. 2012;19(1-2):45-52

Ireneusz GRZYWNOWICZ[1]

POTENTIAL ENVIRONMENTAL MANAGEMENT OF WASTE PRODUCTS FROM EXPLORATORY DRILLING ACTIVITIES

MOŻLIWOŚCI ROLNICZEGO ZAGOSPODAROWANIA PRODUKTÓW ODPADOWYCH Z DZIAŁALNOŚCI POSZUKIWAWCZO-WIERTNICZYCH

Abstract: The investigations were undertaken to assess increasing amounts of waste products generated during drilling and supplied to the soil in respect of potential soil and plant contamination with some elements, and determining the effect of salinization degree on plant growth.

The waste used for pot experiments contained, beside considerable amounts of chlorides, also 18 % of $CaCO_3$ which influenced the increase in chemisorption of fertilizer phosphorus. The deposit supplied to the soils almost 14-times increased the quality of exchangeable sodium. Salinization effect was apparent primarily for red fescue emergences, which were irregular and obviously delayed as the waste was added to the pot. The differences in plant appearance diminished during the vegetation. The largest waste supplement caused a decline in red fescue yield cultivated immediately after its addition.

The effect of waste supplement on increase in salinization became visible only when the highest, 40 % supplement was added and led to slight soil degradation due to salinization (over 2 mS · cm^{-1}).

Keywords: exploratory drilling wastes, plants, sodium and potassium contents, soil salinization

The concept of environmental management of wastes has the best perspective of development. Usability of various wastes for reclamation depends on their chemical and biological properties.

Environmental management of waste products from exploratory drilling activities deposited in spoil pits and previously cleaned of oil derivative compounds still encounters a problem of the waste pollution with heavy metals and excessive salt contents. Therefore, the investigations aimed to assess increasing amounts of waste products originating from spoil pit of a drilling plant located in Witkowice considering potential soil and plant contamination with some toxic elements and to determine the degree of soil salinization on plant growth. For this purpose, plant experiments were

---

[1] Department of Agricultural Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone: +48 12 662 43 48, fax +48 12 662 43 41, email: rrgrzywn@cyf-kr.edu.pl

conducted with increasing supplement of deposit to the soil to observe its effect on plant growth, increasing their contents of some elements and changes of some soil properties.

Materials and methods

The soil used for the experiments revealed properties similar to the one originating from the area adjoining to the landfill.

The following series of experimental design were used: A – soil without deposit supplement, B – soil with 5 % of deposit, C – soil with 10 % of deposit, D – soil with 25 % of deposit, E – soil with 40 % of deposit.

Phosphorus fertilization in $Ca(H_2PO_4)$ form dosed 0.3 g P_2O_5 per pot was applied once prior to the experiment outset. Nitrogen fertilization was applied in a form of NH_4NO_3 in a dose of 0.75 g N per pot on two dates: 0.5 g N per pot before the experiment outset and the remaining part after grass (*Festuca rubra* L.) harvest but before mustard (*Synapis alba* L.) sowing. Because of the soil high abundance in potassium and high content of water soluble potassium in the deposit, no potassium was included in the fertilizer dose. Chemical composition of plants was assessed by means of dry mineralization at 450 ^{o}C for 5 hours. Total contents of nutrients and heavy metals in the soils were determined by digesting the soil in a mixture of HNO_3 and $HClO_4$ (3:2) after incinerating organic substance in a furnace at 450 ^{o}C for 5 hours. The element concentrations in solutions were assessed using ICP method. Because of $CaCO_3$ in the deposit, the soil sorption capacity was determined in NH_4Cl with pH = 8.2 and in the initial, non-carbonate soil with pH = 7.0 following the leaching of water soluble soils with anhydrous ethyl alcohol. The test plant was red fescue grass (*Festuca rubra* L.), Skrzeszowicka c.v., while white mustard (*Synapis alba* L.), Barka c.v., was cultivated as an aftercrop.

Results

A supplement of waste from exploratory-drilling works supplied to the soil affected test plant yielding in the conducted pot experiment. Already 5 % waste addition caused a decline in yield by over 30 % in comparison with the control (Table 1).

Table 1

Plant yielding [g · d.m. per pot]

Fertilizer series	Red fescue			Mustard			Aggregate yield grass + mustard
	AP	R	AP + R	AP	R	AP + R	
A	24.21	4.63	28.84	1.04	0.10	1.14	29.98
B	15.22	3.83	19.05	5.61	0.70	6.31	25.36
C	16.70	3.93	20.63	6.11	0.48	6.59	27.22
D	17.55	3.56	21.11	7.18	0.56	7.74	28.85
E	11.74	2.03	13.77	3.98	0.40	4.38	18.15

Explanation: AP – above-ground parts; R – roots.

However, aggregate yield of both cultivated crops revealed a decrease only by 15 % in this series. In the series with the 10 and 25 % supplements a decrease in yield was even less visible. Only a 40 % admixture of the deposit caused an over 50 % decline in grass yield and 40 % decrease in the aggregate yield of grass and mustard.

The greatest differences in plant growth occurred during the initial period of red fescue vegetation. This fact is confirmed by a regularity described in literature [1, 2], that young plants, mainly at the seedling stage are most sensitive to unfavourable environmental conditions.

The effect of spoil admixture was also noticeable in the chemical composition of the cultivated plants. It was the most pronounced for sodium (almost 5-fold increase in Na concentration) and potassium, where this element content exceeded 6 % in dry matter (Table 2). $CaCO_3$ present in the deposit, beside the effect on the soil reaction, caused an increase in Ca and also Mg content, but to a lesser degree. For calcium the changes were more visible in mustard (Table 3) cultivated as a consecutive crop, which may be due to the time which elapsed from the moment of application.

Table 2

Macroelement contents in red fescue

Series	K		Ca		Mg		Na		P	
	AP	R	AP	R	AP	R	AP	R	AP	R
	$[g \cdot kg^{-1}$ d.m.]									
A	38.9	9.9	1.0	0.4	1.52	0.80	0.54	0.98	3.49	1.54
B	55.1	15.3	5.2	2.6	3.00	2.65	1.34	4.22	1.66	1.22
C	65.8	17.7	4.7	2.4	2.53	3.36	1.55	4.57	1.76	1.00
D	67.2	23.0	2.9	1.7	3.72	3.13	1.32	5.22	1.72	1.01
E	56.1	25.2	1.7	1.6	3.18	3.48	2.60	5.98	2.38	1.23

Table 3

Macroelement contents in white mustard

Series	K		Ca		Mg		Na		P	
	AP	R	AP	R	AP	R	AP	R	AP	R
	$[g \cdot kg^{-1}$ d.m.]									
A	19.5	6.2	11.6	2.7	3.7	0.6	9.00	1.43	3.64	3.71
B	36.4	23.0	17.8	5.7	1.7	1.2	5.94	2.56	2.50	3.35
C	35.1	27.2	21.4	10.2	1.5	1.5	8.03	3.14	2.39	3.49
D	54.0	30.6	22.4	3.1	1.9	1.3	12.51	3.98	2.72	3.34
E	57.9	30.1	20.4	4.6	2.5	1.5	13.02	2.44	3.14	2.37

Considerable changes were detected also in phosphorus content in plants. Calcium carbonate in the deposit affected higher chemisorption of fertilizer supplied to the soil and its concentration in plants was low.

The tendencies of changes in chemical composition were similar in white mustard, although less pronounced as in case of magnesium or phosphorus.

From the perspective of plants cultivated for animal feed not only the absolute quantity of individual nutrients is important, but also their mutual relationships. Adding increasing quantities of deposit to the soil caused a change in proportions between the studied elements. In very acid soil used for the experiments, equivalent ratio K:(Ca + Mg) was much wider (5.7) than the value (2.2) considered optimal [3]. The smallest supplement of the deposit on the level of 5 % contributed to an improvement of fodder quality, whereas narrowing this ratio to the value of 2.8 and further increase of the admixture to the soil led to its considerable widening (Table 4).

Table 4

Changes of K:(Ca + Mg) and (K + Na):(Ca + Mg) equivalent ratios and K:Na and Ca:P weight ratio in red fescue

Series	K:(Ca + Mg)	(K + Na):(Ca + Mg)	K:Na	Ca:P
A	5.71	5.84	72	0.29
B	2.79	2.90	41	3.13
C	3.81	3.97	42	2.67
D	3.82	3.95	51	1.69
E	4.14	4.47	22	0.71

Weight K:Na ratio in red fescue cultivated on all treatments was too wide, which resulted from excessive potassium content in plants. Although the ratio was narrowing with increasing waste admixture, it still exceeded 10:1 proportion. For fodder reasons Ca:P ratio should be on the level of 2:1. Presented data show that 5 % and 10 % waste supplements led to widening this ratio to values considered as proper, but its further growth led to an excessive narrowing of this ratio.

The waste contained great amounts of colloids (71 % of clay particles including 23 % of colloidal clay) and added to the soil caused an increase in its colloidal clay content (Table 5), therefore worsening water-air relationships. Supplying such great quantities of silt fraction to anyway heavy soils favoured creation of reductive conditions in the soil.

The waste used for agricultural management contained over 18 % of $CaCO_3$. Even the smallest (5 %) admixture of the deposit contained over twice more $CaCO_3$ than necessary for the deacidification of the experimental soil. Therefore with increasing deposit addition to the soil growing amounts of $CaCO_3$ remained in free state increasing chemisorption of fertilizer phosphorus. It points to low phosphorus content in plants, despite fertilization with this element.

Significant diversification of soil chemical properties under the influence of liming may affect a decline in yield of crops grown immediately after its application. Gorlach and Gorlach [4] obtained these results while investigating the effect of carbonate forms of calcium and magnesium on yielding of several plant species. A rapid change of exchangeable cation ratios in soil under the influence of applied Ca fertilization observed in the experiments conducted by Czapla and Nowak [5, 6] caused a decrease in the yield of maize and oat from 10 to 15 %. On the other hand, in the studies of Filipek et al [3] conducted on meadows, no response of meadow sward was noted but only when counted as an average for three years. In the first year after liming even several percent decline in yield was registered. The studies of Gorlach and Curylo [7] on liming of two meadows on soils with various granulometric structure yielded different results. In an experiment conducted on light soil with considerable share of exchangeable aluminum in acidity, liming increased yields of meadow sward, whereas in the experiment on very heavy soil ca 10 % decrease in yield occurred.

A negative result of added deposits was elevated soil salinization (Table 5).

Table 5

Changes of some physical and chemical soil properties after experiment completion

Series	% fraction of mm		pH		$CaCO_3$ [%]	C-org [$g \cdot kg^{-1}$]	Salinization [$mS \cdot cm^{-1}$]
	< 0.02	< 0.002	H_2O	KCl			
Waste	71	23	8.99	8.46	18.09	—	4.75
A	41	15	4.92	4.00	nd	8.40	nd
B	41	18	7.14	6.99	0.22	10.40	0.40
C	46	18	7.46	7.07	0.47	10.00	0.86
D	51	20	7.80	7.33	1.85	9.20	1.27
E	59	22	8.00	7.52	4.87	10.60	2.27

Explanation: nd – not determined.

At waste admixtures of between 5 and 10 % the salinization was still slight. The symptoms of weak soil degradation (Table 5) which might have been the reason of a decrease in yield (Table 1) occurred only at 40 % addition of wastes causing a delay of emergences and weakening of growth at the tillering stage.

The cation exchange capacity was assessed in order to establish the effect of deposit added to the soil on changes of exchangeable cation composition in the sorption complex. Data compiled in Table 5 show that the initial soil with the deposit supplement revealed increasing contents of $CaCO_3$ as the amount of added deposit was growing. Therefore, determining the changes of exchangeable cation composition in the sorption complex was conducted in carbonate soils in NH_4Cl with pH = 8.2 whereas for the initial carbonate-less soil using NH_4Cl with pH = 7.0. Acid cations were assessed in an extract of sodium acetate [8]. Because the soils with waste supplement revealed salinization, they were leached with absolute ethyl alcohol.

In each soil there is a small amount of water soluble cations (so called active forms), yet the contents of this form of cations rarely exceed the value of 1 $mmol \cdot kg^{-1}$ of soil [9].

The quantities of individual cations determined in the anhydrous ethyl alcohol may be considered as water soluble forms. The data given in Table 6 show that not only potassium and sodium were present in the sediment as chlorides. Also a small quantity of magnesium and considerable part of calcium occurred in water soluble forms. With deposit supplement increasing from 5 % to 40 % the highest, almost fivefold growth was registered for water soluble sodium. It should be expected that calcium and sodium ions would significantly affect the conditions of plant nutrition in the soil with these wastes admixture.

Table 6

Contents of calcium, magnesium, sodium and potassium cations
in the extract of anhydrous ethyl alcohol

Series	Ca	Mg	K	Na	Total
	$[\text{mmol}(+) \cdot \text{kg}^{-1}]$				
B	15.4	0.56	0.09	3.07	19.12
C	16.6	0.51	0.21	5.60	22.92
D	22.7	0.57	0.14	9.34	32.75
E	26.5	0.69	0.35	14.62	42.16

In the studies by Filipek and Badora [10] conducted on the soil where means for after snow slipperiness control were used, the contents of chloride anions and sodium cations in the 20–40 cm layer was higher by about 0–20 cm, which suggests relatively easy leaching of these ions into deeper soil layers. The soil, on which the pot experiments were conducted belonged to heavy soils, where leaching occurs, though it is weaker.

Ion-exchanging sorption plays an important role is soils in storing and mobilization of nutrients. Determining sorption capacity in soil containing carbonates encounters analytical problems, irrespectively if conducted using indirect method (the sum of individually assessed alkaline cations, eg in ammonium chloride with pH = 8.2), or using a direct method through exchange of sorption complex cations using barium chloride.

As may be seen from the data presented in Table 6, a considerable part of not only sodium but also calcium may occur as water soluble compounds not adsorbed by sorption complex, which will be counted to exchangeable cations.

The waste added to the soil caused deacidification of the very acid, initial soil. After the experiment completion sorption capacity increased over twice, mainly owing to the almost 3-fold growth of the exchangeable calcium and magnesium quantity and over 14-fold increase in the amount of exchangeable sodium. Changes in the quantity of exchangeable potassium were observed only at the 25 % and 40 % waste admixtures. In the presented experiment even at the highest deposit supplement the sum of exchangeable cations K+Na does not exceed 7 %, ie much less than in the salinized soils. Therefore a decrease in yield observed in the conducted experiment already on the treatments with 5 % addition of the waste product should be associated rather with high content of $CaCO_3$ than with the soil salinization, which on these treatments was $0.40 \text{ mS} \cdot \text{cm}^{-1}$.

Table 7

Contents of calcium, magnesium, sodium and potassium cations in an extract of neutral ammonium chloride (series A) and ammonium chloride with pH = 8.2 (series B, C, D and E)

Series	Ca	Mg	K	Na	Total	H	T	V
	$[\mathrm{mmol}(+) \cdot \mathrm{kg}^{-1}]$							[%]
A	125.0	7.87	2.10	1.01	135.98	81.0	216.98	63
B	441.2	17.88	2.14	14.42	475.64	—	475.60	100
C	441.8	18.16	2.77	21.56	484.29	—	484.30	100
D	472.4	25.91	4.14	29.96	532.40	—	532.40	100
E	547.8	40.12	5.48	35.25	628.60	—	628.60	100

The category of degradation which may reveal itself as a decline in yield, particularly of plants sensitive to salinization, is apparent only on the soil with 40 % admixture of waste.

Conclusions

1. Waste product from exploratory drilling activities added to the soil decreased yielding of the test plants cultivated immediately after its introduction to the soil, mainly in the initial period of development.
2. Changes in the plant chemical composition concerned mainly sodium causing almost 5-fold increase in its contents in plants.
3. $CaCO_3$ present in the waste increased chemisorption of fertilizer phosphorus, which limited its bioavailability and decreased its uptake by plants.
4. Increase in the soil salinization became apparent only at the greatest admixture of waste (40 %) causing its slight degradation but the increase in exchangeable sodium did not exceed the values characteristic for salinized soils.
5. A significant amount of mineral colloids present in the waste introduced to heavy soils may lead to worsening of air and water relationships and occurrence of reductive conditions in soil.

References

[1] Pawluśkiewicz B. Zesz Nauk AR Kraków 412 Inżynieria środowiska. 2004;25:171-179.
[2] Grynia M, Grzelak M, Kryszak A. Zesz Probl Post Nauk Rol. 2001;474:263-268.
[3] Filipek J, Skrijka P, Kasperczyk M. Zesz Nauk AR Kraków 120 Rolnictwo. 1977;16:3-17.
[4] Gorlach E, Gorlach K. Roczn Glebozn. 1983;43(3/4):29-43.
[5] Czapla J, Nowak G. Acta Acad Agrocult Tech Olst Agicultura. 1995;61:94–99.
[6] Czapla J, Nowak G. Acta Acad Agrocult Tech Olst Agicultura. 1995;61:101-107.
[7] Gorlach E, Curyło T. Acta Agr et Silv ser Agr. 1987;26:109-120.
[8] Przewodnik do oznaczania pojemności sorpcyjnej gleb. Prace Komisji Naukowych PTG II, Warszawa 1984; 14. 94 p.
[9] Czekała J. Inter. Symposium “Potassium and magnesium in agriculture”, Warszawa-Rogów, 4-6 September 2001;9-10.

[10] Filipek T, Badora A. Roczn Glebozn. 1992;43(3/4):37-43.

MOŻLIWOŚCI ROLNICZEGO ZAGOSPODAROWANIA PRODUKTÓW ODPADOWYCH Z DZIAŁALNOŚCI POSZUKIWAWCZO-WIERTNICZYCH

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

Abstrakt: Celem podjętych badań była ocena wzrastających dodatków do gleby produktów odpadowych powstających w trakcie prowadzenia prac wiertniczych w aspekcie możliwości skażenia gleby i roślin niektórymi pierwiastkami oraz określenie wpływu stopnia zasolenia gleby na wzrost roślin.

Użyty do doświadczeń wazonowych odpad oprócz znacznych ilości chlorków zawierał 18 % $CaCO_3$, który wywoływał wzrost chemisorpcji fosforu nawozowego. Dostarczony do gleby osad zwiększał prawie 14-krotnie ilość wymiennego sodu. Wpływ zasolenia uwidaczniał się przede wszystkim we wschodach kostrzewy czerwonej, które były bardzo nierównomierne i wyraźnie opóźnione w miarę dodatku odpadu do wazonu. W trakcie trwania wegetacji różnice w wyglądzie roślin zmniejszały się. Największy dodatek odpadu powodował spadek plonu kostrzewy czerwonej uprawianej bezpośrednio po jego dodaniu.

Wzrost zasolenia gleby pod wpływem dodatku odpadu uwidocznił się dopiero przy największej jego dawce wynoszącym 40 %, powodując słabą degradację gleby na skutek zasolenia (ponad 2 $mS \cdot cm^{-1}$).

Słowa kluczowe: odpady poszukiwawczo-wiertnicze, rośliny, zawartość sodu i potasu, zasolenie gleby

DOI: 10.2428/ecea.2012.19(01)005 ECOL CHEM ENG A. 2012;19(1-2):53-59

Anna IŻEWSKA[1], Justyna CHUDECKA[2],
Tomasz TOMASZEWICZ[2] and Mariola WRÓBEL[3]

CONTENT OF MACRO- AND MICROELEMENTS IN ROADSIDES' TOP LAYER OF FOREST AREAS AND CHARACTERISTICS OF PLANT SPECIES SETTLED

ZAWARTOŚĆ MAKRO- I MIKROSKŁADNIKÓW W WIERZCHNIEJ WARSTWIE POBOCZA DRÓG TERENÓW LEŚNYCH ORAZ CHARAKTERYSTYKA GATUNKÓW ROŚLIN JE ZASIEDLAJĄCYCH

Abstract: The paper presents research results concerning the content of micro- and macroelements in soils of roadsides along forest areas, salinity indicators and spatial distribution of roadside flora on the basis of trophic index. Study area with the total shoulder width of 8 m, along hardened surface in Szczecin Lowlands. The research has indicated that the content of macro- and microelements: P, K, Mg, Ca and Na was decreasing as the distance from the roadway was growing. Indeed, most of macroelements were found in the edge zone (edge of shoulder), with a width of 20–30 cm, adjacent directly to the edge of roadway. In all researched areas soil richness for phosphorus was low, for magnesium low (A and B zone) and very low (C and D zone), high in potassium in the edge area and medium in the proper shoulder. Content of soluble microelements in 0.5 mol $\cdot$ dm^{-3} HCl was the greatest in the edge area and was decreasing if further from the edge of the roadway. Rating abundance of species observed on the edge of the shoulder (A), on the proper shoulder (B), in roadside ditches (C), on slopes of mid-forest (D) showed a similar number of species found in roadside ditches and on slopes (on average 23 and 22 taxons). On the basis of soil salinity indicators (Z and *SAR*) they were not specified in any of the analyzed shoulder zones.

Keywords: forest soils, the content of macro- and microelements in the soil, flora, forest, soil salinity indicators.

Soil salinity, which is caused by ice-removing chemicals used on streets in urban areas, is formed along traffic routes, where sodium chloride has been used in order to improve transport during Winter since 1986. These actions, which we are not able to avoid, cause cyclic accumulation of large amount of soluble salts, mainly NaCl and

---

[1] Department of Sanitary Engineering, West Pomeranianian Technological University, al. Piastów 50, 70–311 Szczecin, Poland, phone: +48 91 449 77 49, email: anna.izewska@zut.edu.pl

[2] Department of Soil Reclamation and Enviromental Chemistry, West Pomeranianian Technological University, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, phone: +48 91 449 63 61, emai: justyna.chudecka@zut.edu.pl

[3] Department of Botany and Nature Protection, West Pomeranianian Technological University, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, phone: +48 91 449 63 13, email: mariola.wrobel @zut.edu.pl

$NaHCO_3$, especially in early Spring, which increases salt concentration and pH of the soil to the level which may be toxic for plants. Hence, a solution is sought, which would assure both smoothness of traffic and would be less harmful to the environment, as well as to road users. In Finland in the late 90's potassium formate (HCOOK) and potassium acetate (CH_3COOK) were used. In the USA are used as follows: magnesium acetate [(CH_3COO_2)Mg], calcium acetate [(CH_3COO_2)Ca], sugar-rich solutions produced during partial hydrolysis of waste products from processing of sugar beet and maize, urea $CO(NH_2)_2$ and alcohols [1].

Ice-removing chemicals used on streets have an impact on chemical nature of roadsides' top layers, and thus roadside flora. Their influence is connected to properties of substrate material, as well as the distance from the roadway.

The aim of this paper is to access changes in content and richness category of forms acknowledged as assimilable macro- and microelements in roadside soil along forest areas in Szczecin Lowlands during Spring time, changes in indicators of soil salinity and participation of plant species with different trophic index.

Material and methods

In Spring 2005, research was carried out in order to study roadsides with hardened surface (asphalt) and with comparable capacity, located along forest areas of Szczecin Lowlands.

For the purpose of observation four sample collection points were chosen, located outside build-up areas along forest roads: Modrzewie 53°34′26″N, 014°47′09″E, Lozienica 53°33′03″N, 014°36′32″E, Kliniska 53°27′44″N, 014°47′36″E and Strumiany 53°27′08″N, 014°52′12″E.

Sampling from the top layer of humus 0–10 cm of roadside was performed in Spring (March) in each sample collection point. Four characteristic roadside zones were researched, situated as follows:

A – road shoulder edge adjoining the road surface (0.2–0.3 m width),
B – proper road shoulder (1.0–1.2 m width),
C – ditch (1.0–1.5 m width, 0.5–0.8 m depth),
D – slope (1.0–2.5 m height, inclination 30°).

Using methods generally accepted in soil science, determinations were done as follows: granulation, soil pH reaction measured in KCl solution of 1 mol · dm^{-3} (pH_{KCl}) concentration and loss on ignition at 550 °C. Content of forms regarded as available to plants, after extraction with HCl at a concentration of 0.5 mol · dm^{-3} [2], was determined by AAS: K, Ca Mg, Na, Cu, Fe, Mn and Zn while P colorimetrically.

Soil salinity was calculated on the basis of degree of changes in soil sodium (Z) relative to the amount of sodium ions of calcium and magnesium ions expressed in equivalent amounts [3], and SAR (*Sodium Adsorption Ratio*) [4]:

$$Z = \frac{\mathrm{Na}}{\mathrm{Ca} + \mathrm{Mg}},$$

$$\mathrm{SAR} = \frac{\mathrm{Na}}{\sqrt{\frac{\mathrm{Ca} + \mathrm{Mg}}{2}}}$$

The significance of differences in element content between zones was determined by using Tukey's HSD test, while the SD value at 0.05 significance level test of Newman-Keulus, using the program Statistica 9.

The assessment of soil was carried out according to the classification of Sapek and Sapek [2], which is applied to agricultural grasslands. Because the tested samples contained less than 20 % of organic matter, classification of the nutrient content was made, which divided soil richness into three grades: low, medium and high. The exceptions was magnesium, which content was valued for five grades of abundance.

Results and discussion

Data included in Table 1, characterizing researched soil, were already presented in earlier publications [5, 6]. Re-presentation was necessary to assess soil fertility.

Researched soil had granulation of loose sand according to PTG classification [7]. $\mathrm{pH_{KCl}}$ values allowed to determine that in A and B zones the reaction was neutral and in C and D zones it was acid. Salinity as well as loss on ignition were decreasing as the distance from the edge of the road was further [5].

Table 1

The mean value of chosen properties in the 0–10 cm layer of mid-forest sideroads in Spring

Roadside zone	Loss on ignition [%]	$\mathrm{pH_{KCl}}$	Salinity [g NaCl $\cdot$ kg^{-1} of soil]	Percentage content of fractions with diameter [mm]			
				> 2	2–0.5	0.5–0.002	< 0.002
A	2.96	7.03	0.202	17.2	93.3	5.3	1.4
B	2.15	6.70	0.183	4.8	93.3	4.8	1.9
C	2.20	5.20	0.131	1.7	92.6	5.1	2.2
D	1.80	5.20	0.096	1.1	93.6	4.7	1.7

The content of all researched macroelements (P, K, Mg, Ca and Na), was decreasing as the distance from the edge of the road was further. Significant changes were found between soils of different zones (Table 2). The highest content of phosphorus soluble in 0.5 mol $\cdot$ dm^{-3} HCl was in the shoulder area (3.30 mg $\cdot$ 100 g^{-1} soil) and as one moves from the edge of the road it was significantly decreasing in the zone of the ditch and embankment. That same relation appeared in the case of soluble potassium in soil.

Phosphorus content was established low. Potassium content in A zone was high, in B zone medium, and in zones C and D it was low. Magnesium in A and B zones is low, and in C and D zones very low. According to Bieniek [8], almost 1/3 of magnesium in total is present in mineral compounds in soluble forms. In studies of muck soil conducted by the authors, the content of magnesium according to boundary numbers reached very low level, which is a proof for the strong need of fertilizing soils researched.

Table 2

The average content of macro- and microelements soluble in 0.5 mol · dm^{-3} HCl in 0–10 cm layer of soil from the roadsides and homogenous groups

Shoulder zone	P	K	Mg	Ca	Na	Cu	Fe	Mn	Zn	Soil salinity indicator	
	[mg · 100 g^{-1} of soil]					[mg · kg^{-1} of soil]				Z	*SAR* (*Sodium Adsorption Ratio*)
A	3.30a	43.9a	39.9a	5.80a	0.358a	14.80a	14.71a	115.0	68.1a	0.0078a	0.071
B	2.59ab	26.5ab	25.4ab	5.05ab	0.229ab	6.90	12.04ab	76.9	55.1ab	0.0075	0.054
C	1.98bc	16.2b	11.8b	2.08ab	0.068b	4.23	6.51ab	55.5	36.7b	0.0049	0.024
D	1.49c	10.9b	9.2b	1.32b	0.043b	1.32	5.20b	46.7	31.2b	0.0041	0.018
$NIR_{(0.05)}$	1.08	24.4	18.8	3.94	0.214	n.i.	8.59	n.i.	28.7	—	—

Among other microelements, copper content showed no relevant diversity, despite the fact that in A and D zones the content was high, in B zone medium, and in D zone low. Moreover, manganese also showed no important variety, even though A zone had medium content and the rest had low. In case of iron there was a significant difference between zones A and D, although the content of zinc was high, there was an essential difference between the soils of zone A and soils of zones C and D (Table 2).

Soil salinity indicators Z and *SAR* are not equivalent. Both allow for assessment of environmental risks associated with soil environment connected to content of soluble salts of sodium [3]. In the study, the Z rate was less than 1, which indicates a lack of signs of salinity. The value of this index ranged from 0.0078 to 0.0041. Also the *SAR* index was less than 10, so the soil has appropriate conditions for the development of plants (Table 2). It was observed that the further from the roadway, the lower was the value of indexes researched.

Rating the number of species observed on the edge of the road shoulder (A), on the proper road shoulder (B), in ditches (C), and on slopes (D), it showed a similar number of species found in roadside ditches and on slopes (on average 23 and 22 taxons).

In further zones of the road shoulder, which were situated next to road surface, the most species were recorded on the proper road shoulder (on average 19 taxons),while the road shoulder edge stood a small number of observed taxons (on average 7). Analysis of *trophism index* (Tr) based on ecological index numbers [9] showed a domination of species preferring mesotrophic soils (Tr = 3) and oligotrophic (Tr = 2) throughout the whole profile of vertical formation of mid-forest roadsides in the researched area. In this respect, two became distinguished – a roadside ditch and embankment, where the species accounted for more than 83 % and 86 % of all plants observed there. Among them *Rumex acetosella*, *Festuca ovina*, *Helichrysum arenarium*, *Hieracium pilosella*, *Corynephorus canescens*, *Trifolium campestre*, *Jasione motana*, *Calluna vulgaris*, *Vaccinium myrtillus*, *Artemisia campestris* and *Calamagrostis epigejos* were most often reported (Fig. 1). In both of these zones single plant species

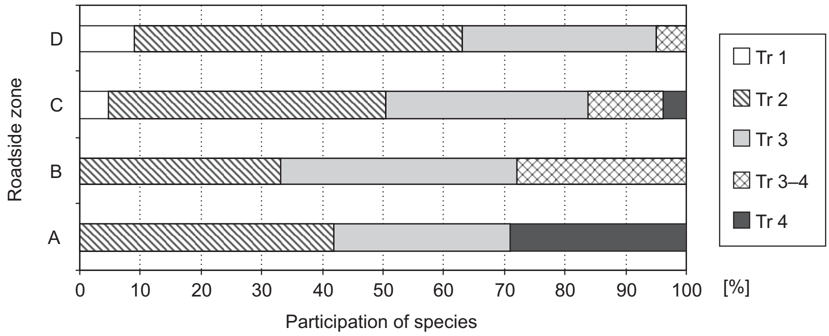

Fig. 1. The percentage of species at different trophic index by Zarzycki [9], in particular zones of mid-forest roadsides. Key: A – edge of shoulder; B – proper shoulder; C – roadside ditch; D – roadside slope; Tr 1 – extremely oligotrophic soils; Tr 2 – oligotrophic soils; Tr 3 – mesotrophic soils; Tr 3–4 – meso- to eutrophic soils; Tr 4 – eutrophic soils

associated with extremely oligotrophic habitats (Tr = 1) were observed, such as *Trifolium arvense*, *Sedum acre or Vaccinium vitis-idea*.

While in proper road shoulder of mid-forest roads and its edge presence of species associated with mesotrophic and oligotrophic soils was of a lesser degree and amounted to 73 % and 71 %, the most frequently observed taxons were as follows: *Carex arenaria*, *Carex hirta*, *Agrostis vulgaris*, *Trifolium campestre*, *Cerastium arvense*, *Holcus mollis*, *Veronica officinalis* and *Festuca rubra*. Presence of intolerant species to extremely oligotrophic habitats was not stated, whereas observed were the species which indicated on eutrophic nature of substrate, such as *Plantago major* or *Poa annua*.

Conclusions

1. The content of forms regarded available for plant macroelements P, K, Mg, Ca and Na in soil was decreasing as the distance was further from the edge of the roadway. Indeed, most macroelements was in the edge zone (edge of shoulder), with a width of 20–30 cm, adjacent directly to the edge of the roadway.
2. In all researched areas soil richness for phosphorus was low, for magnesium low (A and B zone) and very low (C and D zone), high in potassium in the edge area and medium in the proper shoulder.
3. Content of soluble microelements in 0.5 mol · dm^{-3} HCL was the greatest in the edge area and was decreasing if further from the edge of the roadway.
4. Analysis of trophic index leads to the conclusion that in the whole profile of vertical formation of roadsides species preferring mesotrophic soils (Tr = 3) and oligotrophic soils (Tr = 2) were clearly dominating. However, at a distance of 2 m from the road (edge of shoulder and proper shoulder) species preferring eutrophic soils and in more distant soils (ditch and slope), plants preferring extreme oligotrophic habitats were observed.
5. Shoulder zones differed in abundance of species observed. The largest – with similar taxons number was found in roadside ditches (C) and on slopes of mid-forest roads (D) (on average 23 and 22), on the proper shoulder (B) were slightly less species (19), while on the edge of the shoulder (A) the number of taxons decreased to 7.

References

[1] Kochanowska K, Kusza G. Wpływ zasolenia na właściwości fizyko-chemiczne gleb Opola w latach 1994 i 2009. Inż Ekol. 2010;23:14-21.

[2] Sapek A, Sapek B. Metody analiz chemicznych gleb organicznych. Mat Instr IMUZ. Falenty. 1997;81.

[3] Gołda T. Rekultywacja. Uczelniane Wyd. Naukowo-Dydaktyczne AGH, Kraków: 2005.

[4] Treder W. Jakość wody do nawadniania i filtrowania. Szkółkarstwo nr 5, Plantpress: 2004.

[5] Wróbel M, Tomaszewicz T, Chudecka J. Floristic diversity and spatial distribution of roadside halophytes along forest and field roads in Szczecin lowland (west Poland). Polish J Ecol. 2006;54(2):303-309.

[6] Chudecka J, Tomaszewicz T, Pacewicz K, Wróbel M. Wybrane właściwości chemiczne powierzchniowej warstwy gruntów przydrożnych w okresie wiosny i jesieni. Folia Pomeranae Univ Technol Stetin. 2010;14:49-56.

[7] PTG 2008:www.ptg.sggw.pl/images/Uziarnienie_PTG_2008.pgf.pdf

[8] Bieniek B, Karwowska J, Bieniek A. Właściwości chemiczne ekstensywnie użytkowanych gleb murszowych na torfowisku "Siódmak", Rocz Glebozn. 2007;57(1/2):12-23.
[9] Zarzycki K, Trzcińska-Tacik H, Różański W, Szeląg Z, Wołek J, Korzeniak U. Ekologiczne liczby wskaźnikowe roślin naczyniowych Polski Instytut Botaniki PAN, Kraków: 2003.

ZAWARTOŚĆ MAKRO- I MIKROSKŁADNIKÓW W WIERZCHNIEJ WARSTWIE POBOCZA DRÓG TERENÓW LEŚNYCH ORAZ CHARAKTERYSTYKA GATUNKÓW ROŚLIN JE ZASIEDLAJĄCYCH

Katedra Inżynierii Sanitarnej
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

Abstrakt: Przedstawiono wyniki badań dotyczące zawartości makro- i mikroskładników w glebach poboczy dróg biegnących przez tereny zadrzewione, wskaźników ich zasolenia oraz przestrzennego rozmieszczenia flory przydrożnej na podstawie wskaźnika trofizmu. Badaniami objęto strefy pobocza o łącznej szerokości 8 m, wzdłuż dróg o nawierzchni utwardzonej na Nizinie Szczecińskiej. Przeprowadzone badania wskazują, że zawartość makroskładników: P, K, Mg, Ca oraz Na zmniejszała się w glebie w miarę oddalania się od krawędzi jezdni. Istotnie najwięcej makroskładników było w strefie brzegowej (skraj pobocza), o szerokości 20–30 cm, przylegającej bezpośrednio do krawędzi jezdni. Analizując zasobność gleby w przyswajalny fosfor, stwierdzono, że była ona niska we wszystkich badanych strefach, magnezu niska (strefa A i B) i bardzo niska (strefa C i D), a potasu wysoka w stresie brzegowej i średnia w strefie pobocza właściwego. Zawartość mikroskładników rozpuszczalnych w 0,5 mol $\cdot$ dm^{-3} HCl największa była w strefie brzegowej i zmniejszała się w miarę oddalania od krawędzi jezdni. Ocena liczebności gatunków obserwowanych na skraju pobocza (A), na poboczu właściwym (B), w przydrożnych rowach (C) i na skarpach dróg śródleśnych (D) wykazała podobną liczbę gatunków występujących w przydrożnych rowach i na skarpach (średnio 23 i 22 taksony). Na podstawie wskaźników zasolenia gleby (*Z i SAR*) nie określono ich w żadnej z analizowanych stref pobocza.

Słowa kluczowe: gleby leśne, zawartość makro- i mikroskładników w glebie, flora leśna, wskaźniki zasolenia gleby

DOI: 10.2428/ecea.2012.19(01)006 ECOL CHEM ENG A. 2012;19(1-2):61-68

Monika JAKUBUS[1], Zbigniew KACZMAREK[1]
and Agnieszka WOLNA-MARUWKA[2]

CHANGES OF SOME SELECTED SOIL PROPERTIES INCUBATED WITH THE ADDITION OF AGAR, STARCH AND EFFECTIVE MICROORGANISMS

ZMIANY WYBRANYCH WŁAŚCIWOŚCI GLEBY INKUBOWANEJ Z DODATKIEM AGARU, SKROBI I EFEKTYWNYCH MIKROORGANIZMÓW

Abstract: From among increasing numbers of various ecological solutions which are applied in traditional farming, considerable usefulness of the Effective Microorganism (EM) technology is frequently indicated. This preparation is believed to exhibit a wide spectrum of activities both in plant as well as in animal production. It has been demonstrated that after soil application of the discussed preparation, mineralisation and humification processes of organic compounds are accelerated. Possible changes in soil chemical properties which could occur following the application of this conditioner continue to remain debatable.

In the light of the above, investigations were undertaken with the aim to determine the impact of EM on selected physicochemical and chemical soil properties. The above tasks were realised with the assistance of an incubation experiment employing Phaeozems inoculated with EM to which increasing doses of agar or starch were added.

The obtained data revealed that the application of EM with polysaccharides can exert different effects on the examined soil properties. No statistically significant influence was observed with regards to the majority of the examined physicochemical properties. Quantitative changes of macro- and microelements depended on the type of the applied polysaccharide and its dose.

Keywords: effective microorganisms, agar, starch, physicochemical and chemical soil properties

Contemporary agriculture is looking for cheap but, at the same time, effective and environmentally-friendly methods of enhancing soil fertility and increasing yields of crop plants. That is why agricultural practice is getting increasingly interested in natural, biological preparations such as *Effective Microorganism* (EM). It is a composition of over 80 genetically unchanged microorganisms in which bacteria (photosynthetic and lactic acid), yeasts, actinomycetes and fermenting fungi dominate.

---

[1] Department of Soil and Ground Protection, Poznan University of Life Sciences, ul. Szydłowska 50, 60–656 Poznań, Poland, phone: +48 61 848 73 88, email: monja@up.poznan.pl

[2] Department of Microbiology General and Environmental, Poznan University of Life Sciences, ul. Szydłowska 50, 60–656 Poznań, Poland, email: amaruwka@up.poznan.pl

According to Higa [1], the mastermind behind this microbiological mixture as well as Sheng et al [2] and Woodwad [3], such selection of microorganisms in practice guarantees its high and advantageous impact on the environment. With respect to soil, the argument is to improve soil fertility and health condition. This finds expression in the intensified enzymatic and biological soil activity as well as in favourable changes in its chemical and physicochemical properties. The EM impact manifests itself in a faster rate of mineralisation-humification transformations of organic matter which frequently result in increased quantities of organic carbon [4, 5].

Many experiments confirming a positive influence of EM on soils and plants were carried out in such countries as: Pakistan, Indonesia, Philippines, Thailand, China. However, the reliability of these results is frequently questioned due to the short duration of these trials as well as their local nature [6]. However, despite serious doubts, EM preparations continue to gain in popularity not only in Japan and the USA where they find many supporters but also in Europe, including Poland [7]. It is clear from the review of literature [7] on the subject that the main focus of attention of Polish researchers appears to concentrate on the determination of the influence of EM on the health and yields of crop plants. Much less attention is paid to the assessment of EM impact on soil physicochemical and chemical properties.

In order to elucidate this problem, experiments were undertaken the aim of which was to carry out investigations on changes of selected soil properties which took place following the soil incubation with EM-A preparation and two polysaccharides intended to enhance the effectiveness of microorganisms introduced into the soil.

Material and methods

The assumed research objective was realised on the basis of soil samples derived from an incubation experiment carried out for the period of 5 months in controlled conditions of temperature (± 22 ^{o}C) and air humidity (± 60 %). In the performed experiments Phaeozems was used which was sprayed with the EM-A preparation at a rate corresponding to 100 dm^3 per hectare. Since no changes were observed in soil properties before and after the treatment with the EM-A preparation, the study presents results referring only to the soil incubated with EM treating it as a control combination. The soil which was sprayed with EM-A was supplemented with three doses of agar (A) and starch (S) corresponding to 100 (dose 1), 200 (dose 2) and 1000 kg (dose 3) per hectare. Therefore, the experimental design comprised the following combinations:

K1 – Phaeozems incubated with EM-A preparation;
K2 – Phaeozems incubated with EM-A preparation and with agar at dose 1;
K3 – Phaeozems incubated with EM-A preparation and with agar at dose 2;
K4 – Phaeozems incubated with EM-A preparation and with agar at dose 3;
K5 – Phaeozems incubated with EM-A preparation and with starch at dose 1;
K6 – Phaeozems incubated with EM-A preparation and with starch at dose 2;
K7 – Phaeozems incubated with EM-A preparation and with starch at dose 3;

The following physicochemical properties were investigated in the soil samples collected from the above-presented combinations: *soil reaction* (pH), *hydrolytic acidity*

(Hh), *total base cations* (S), *cation exchange capacity* (CEC). CEC was calculated on the basis of Hh and S values using the following formula: PWK = Hh + S.

The following parameters were determined from among chemical soil properties: *content of organic carbon* (C_{org}) and *total nitrogen* (N_{tot}), amounts of available for plants macroelements (N mineral, P, K, Mg and $S\text{-}SO_4$) and microelements (Cu, Mn, Zn, Fe). The above properties were determined with the assistance of methods commonly applied in soil science analyses; their detailed descriptions can be found in Jakubus [8]. Data presented in this study are means of three replicates. The obtained results were subjected to formal evaluation with the assistance of the analysis of variance for single-factorial experiments using F test at the level of significance p = 0.95. The smallest significant differences were calculated using Tukey method at the level of significance of $\alpha = 0.05$ and then uniform groups within the factor level were established.

Results and discussion

Literature data indicate that the application of EM resulted in the improvement of plant health condition [9–11] or led to the increase in their yields [12–15]. Reports referring to the EM impact on soil chemical and biochemical properties are less unequivocal. On the one hand, the literature on the subject corroborates such influence [4, 16] and, on the other, denies it [17, 18]. In such circumstances, Badura [19] maintains that advantageous effects of EM activities can best be seen in conditions of degraded, poor and neglected soils where microbiological balance is disturbed. The arguments of the above researcher can be referred to the performed experiment. The soil used in the trial was not degraded and, probably, this is why the obtained results failed to confirm unambiguously a positive impact of EM on properties of the examined soil. Irrespective of the applied polysaccharide, directions of changes of the examined soils were similar. As evident from Table 1, soil sorption properties described by absorbing capacity values (CEC) as well as total base cations (S) did not undergo significant changes under the influence of the applied doses of agar and starch.

Table 1

Influence of experimental factors on quantitative changes of physicochemical properties

Combinations	pH	Hh [mmol $H^+ \cdot kg^{-1}$]	S [mmol $\cdot kg^{-1}$]	CEC [mmol $\cdot kg^{-1}$]
1	6.7	4.65c ± 0.21	221.48 ± 3.34	226.13 ± 3.55
2	6.7	6.77a ± 0.25	210.52 ± 9.80	217.29 ± 10.05
3	6.8	6.22ab ± 0.32	226.47 ± 0.26	232.69 ± 0.06
4	6.8	5.66b ± 0.46	221.97 ± 3.07	227.63 ± 2.61
5	6.7	6.37ab ± 0.32	230.38 ± 20.69	236.76 ± 21.01
6	6.7	6.19ab ± 0.58	220.09 ± 6.03	226.28 ± 6.61
7	6.7	5.66b ± 0.90	221.67 ± 9.23	227.33 ± 8.34
LSD	*n.s.*	*0.961*	*n.s.*	*n.s.*

± SD

Neither was the soil reaction found to have been significantly changed by the experimental factor as its pH value remained on the same level. These results appear to contradict literature data which indicate a positive EM impact on pH value increase which was accompanied by declining soil acidification (Hh) and increased value of the soil sorption capacity (CEC) [4, 5, 20]. From among physicochemical soil properties analysed in the study, only the values of hydrolytic acidity varied. Together with the increase of agar or starch doses, soil Hh values were found reduced from 6.77 (K2) to 5.66 mmolH · kg^{-1} (K4) or from 6.37 (K5) to 5.66 mmol H · kg^{-1} (K7) (Table 1). Despite this, soil supplementation with polysaccharides led to its acidification as evidenced by higher Hh values in comparison with those found in the control soil (4.65 mmol H · kg^{-1}).

It is assumed that the aim of the EM introduction into the soil is, among others, to stimulate quantitative changes of humus [5, 20, 21]. Such phenomenon was confirmed also by Valarini et al [4] who reported 2.5–3.0 fold C_{org} in loamy soil following EM application. However, the reports of the above-mentioned researchers were not corroborated by the results of our investigations because neither the C_{org} nor humus content changed in a manner statistically significant after the addition of polysaccharides to the soil sprayed with EM-A. As evident from the data in Table 2, irrespective of the experimental combination, the amount of C_{org} ranged from 8.39 (K2) to 10.85 mg · kg^{-1} (K5) and that of humus – from 14.48 (K2) to 18.70 g · kg^{-1} (K5).

Table 2

Influence of experimental factors on quantitative changes of basic chemical properties

Combinations	C_{org}	Humus	N_{tot}	N-NH_4	N-NO_3
	[g · kg^{-1}]		[mg · kg^{-1}]	[mg · kg^{-1}]	
1	9.47 ± 1.5	16.33 ± 2.7	1165.5a ± 24.74	7.7 ± 0	4.55cd ± 0.49
2	8.39 ± 1.5	14.48 ± 2.7	1088.5c ± 4.94	7.63 ± 1.09	7.45a ± 0.63
3	9.60 ± 0.3	16.55 ± 0.5	1151.5ab ± 34.64	7.7 ± 0.99	6.30b ± 0.99
4	9.73 ± 0.3	16.77 ± 0.5	1092.0bc ± 0	8.05 ± 0.49	4.55cd ± 0.49
5	10.85 ± 0.1	18.70 ± 0.2	1144.5abc ± 64.34	7.35 ± 0.49	4.8cd ± 0.14
6	10.06 ± 0.4	17.35 ± 0.8	1148.0abc ± 9.90	7.0 ± 0.99	3.85d ± 0.49
7	9.85 ± 0.1	16.97 ± 0.3	1114.0abc ± 28.28	7.45 ± 0.35	5.45bc ± 0.21
LSD	*n.s.*	*n.s.*	*61.80*	*n.s.*	*1.102*

± SD

The chemical element closely integrated with soil humus compounds is nitrogen. According to Valarini et al [4], total nitrogen content in loamy soil treated with EM may increase even by up to 45–65 %. In our own experiments, a reverse direction of total nitrogen quantitative changes was observed. The interaction between the EM-A preparation and added polysaccharides resulted in a decline in the amount of this constituent in comparison with the content determined in the control soil (Table 2).

With respect to mineral nitrogen forms, only differences in the N-NO_3 content in the soil from the experimental combination were statistically significant. Quantitative

$N\text{-}NO_3$ changes depended on the polysaccharide added to the soil. In conditions of increasing agar doses, the content of this form of nitrogen was found to decrease from 7.45 (K1) to 4.55 $mg \cdot kg^{-1}$ (K3). At the same time, it should be stated that – against its amount determined in the control soil – agar doses of 100 and 200 kg/ha caused 1.5 fold and 38 % higher $N\text{-}NO_3$ content in soils of combination No. 2 and 3, respectively. On the other hand, in conditions of the soil incubated with EM-A and starch, quantities of the discussed form of mineral nitrogen comparable to those found in the control soil were determined (Tab. 2). Irrespective of the experimental combination, concentrations of $N\text{-}NH_4$ in soil ranged from 7.35 (K5) to 8.05 $mg \cdot kg^{-1}$ (K4) (Table 2).

From the point of view of agricultural practice, available forms of macro- and microelements are of key importance for plant nutrition and there is no agreement in the literature on the subject regarding this issue. Zydlik and Zydlik [5] reported smaller quantities of available phosphorus, potassium, magnesium as well as mineral nitrogen in the soil spread with the EM solution. On the other hand, Paschoal et al [20] failed to observe any influence of the applied EM preparation on concentrations of available macroelements.

From among the analysed macroelements, quantities of available phosphorus and magnesium were characterised by low variability in the examined experimental soil samples. A common feature of these constituents was that their quantities in the soil were found to decline together with growing agar doses, while with the increase of the starch dose, these quantities also increased (Table 3). Against this background, it is worth emphasising distinct changes in quantities of sulphur and potassium. Following the addition to the soil of growing agar doses, sulphate sulphur quantities were also found to grow, whereas increasing doses of starch were accompanied by decreasing content of this constituent. As to the content of $S\text{-}SO_4$ in the control soil (49.86 $mg \cdot kg^{-1}$), respectively 25 % more and 30 % less of this form were determined in the soil incubated with the highest doses of agar (K4) and starch (K7) (Table 3). Regardless of the type of polysaccharide added to the soil, quantities of plant available K decreased and were by 18 % lower in relation to the content of this constituent determined in the control sample (Table 3).

Table 3

Influence of experimental factors on quantitative changes of available for plants macroelements [$mg \cdot kg^{-1}$]

Combinations	K	P	Mg	S
1	282.00a ± 4.66	259.63a ± 14.83	98.61a ± 1.96	49.86b ± 5.49
2	262.21a ± 7.44	237.12a ± 1.81	91.67b ± 1.96	35.21c ± 1.86
3	230.07b ± 2.72	270.89b ± 6.15	90.28bc ± 1.96	53.54b ± 3.71
4	232.87b ± 15.54	248.63b ± 13.02	87.50c ± 1.96	62.30a ± 0.52
5	277.13a ± 3.93	216.29a ± 2.00	87.50c ± 0	49.33b ± 0
6	224.42b ± 13.99	246.33b ± 29.30	91.67b ± 1.96	37.99c ± 3.71
7	232.11b ± 29.84	239.68b ± 19.17	95.83a ± 0	35.06c ± 7.42
LSD	*28.159*	*30.374*	*3.274*	*8.047*

± SD

A direction of quantitative macroelement changes in the soil sprayed with the EM-A solution similar to that indicated above was reported by Zydlik and Zydlik [5] and, in their opinion, it should be attributed to the uptake of nutrients by plants. There was no plant factor in our own investigations and, therefore, the obtained results may point to a process of immobilisation of macroelements. Such possibility, especially with reference to biogenic components, was indicated by Freney et al [22] and Goh and Gregg [23]. According to the above researchers, in conditions of increased water content and carbon concentration, immobilisation of macroelements occurs more intensively.

From among the analysed microelements, manganese and iron quantitative changes in the examined soil were not corroborated statistically. Contents of the zinc and copper underwent similar changes under the influence of the experimental factor. As evident from data presented in Table 4, in comparison with the quantities of Zn and Cu in the control soil, in conditions of soils supplemented with agar or starch, their quantities were slightly higher. Therefore, in the case of soil incubated with EM-A and the highest dose of agar, the determined amounts of Zn and Cu were by, respectively, 46 % and 23 % lower. On the other hand, in the case of the soil incubated with EM-A and increasing quantities of starch, the determined quantities of Zn and Cu were by, respectively, 14 % and 31 % lower (Table 4). The increasing doses of starch did not differentiate the content of Cu at a simultaneous increase of zinc quantitative levels. On the other hand, increasing doses of agar were accompanied by a decline in the content of Zn (38 %) and Cu (17 %) (Table 4).

Table 4

Influence of experimental factors on quantitative changes of available for plants microelements [mg · kg^{-1}]

Combinations	Mn	Zn	Cu	Fe
1	71.70 ± 4.81	8.83a ± 1.28	1.60a ± 0.35	771.42 ± 7.82
2	75.10 ± 3.85	7.63b ± 0.43	1.48ab ± 1.17	773.80 ± 6.61
3	64.89 ± 0.96	6.37d ± 0.21	1.23ab ± 0.17	775.10 ± 6.92
4	73.06 ± 0.96	4.76e ± 2.34	1.23ab ± 0.17	773.58 ± 4.77
5	70.34 ± 0.96	6.75cd ± 0.64	1.11b ± 0	780.0 ± 0
6	74.42 ± 0.96	7.02bc ± 0.43	1.11b ± 0	780.0 ± 0
7	68.98 ± 12.51	7.62b ± 1.28	1.11b ± 0.35	780.0 ± 0
LSD	*n.s.*	*2.30*	*0.43*	*n.s.*

± SD

Conclusions

The results of our investigations prove that it is not possible to question explicitly the joint action of EM and polysaccharides on physicochemical and chemical properties of the examined soil. The incubation of soil with the EM-A preparation and polysaccharides influenced mainly its chemical properties. Their changes depended on the type of the added polysaccharide as well as on its dose. Increasing doses of agar added to the soil with the EM-A preparation reduced the content of available macro- and microelements. The joint action of the increasing quantities of starch doses and EM in the soil resulted in higher quantities of the examined components.

References

[1] Higa T. Effective Microorganisms: A New Dimension for Nature Farming. Proc Second Int. Conf. on Kyusei Nature Farming. Washington, USA: 1994;20-22.

[2] Sheng Z, Chaohai W, Chaodeng L, Haizhen W. Damage to DNA of effective microorganisms by heavy metals: Impact on wastewater treatment. J Environ Sci. 2008;20:1514-1518.

[3] Woodward D. Effective microorganisms as regenerative systems in earth healing. www.living-soil.co.uk./learning/soilsustain.htm. 2003.

[4] Valarini PJ, Diaz Alvarez MC, Gasco JM, Guerrero F, Tokeshi H. Assessment of soil properties by organic matter and EM – microorganism incorporation. Rev Brasil Cience Solo. 2003; 27:519-525.

[5] Zydlik P, Zydlik Z. Impact of biological effective microorganism (EM) preparations on some physico-chemical properties of soil land vegetative growth of apple-tree rootstocks. Nauka Przyr Technol. 2008;2:1-8.

[6] Condor-Golec AF, Perez PG, Lokare Ch. Effective Microorganisms: Myth or reality? Rev Peru Biol. 2007;14(2) 315-319.

[7] Janas R. Możliwości wykorzystania efektywnych mikroorganizmów w ekologicznych systemach produkcji roślin uprawnych. Probl Inż Roln. 2009;3:111-116.

[8] Jakubus M. Wybrane zagadnienia z gleboznawstwa i chemii rolnej. Poznań: Wyd. Uniwersytet Przyrodniczy; 2010.

[9] Boligłowa E. Ochrona ziemniaka przed chorobami i szkodnikami przy użyciu Efektywnych Mikroorganizmów (EM) z udziałem ziół. In: Wybrane zagadnienia ekologiczne we współczesnym rolnictwie. Zbytek Z., editors. Poznań: PIMR; 2005;165-170.

[10] Boligłowa E, Gleń K. Assessment of effective microorganisms activity (EM) in winter wheat protection against fungal diseases. Ecol Chem Eng A. 2008;15(1-2):23-27.

[11] Górski R, Góra K. Wpływ efektywnych mikroroganizmów (EM) na rozwój in vitro grzyba Trichoderma Harzianum występującego w uprawie pieczarki dwuzarodnikowej (Agaricus bisporus). Post Ochr Rośl. 2009;49(4):2005-2008.

[12] Piskier T. Reakcja pszenicy jarej na stosowanie biostymulatorów i absorbentów glebowych. J Appl Agricult Eng. 2006;51(2):136-138.

[13] Gajda A, Igras J. Określenie produkcyjnych i ekologicznych skutków stosowania preparatu WM-A w uprawie zbóż i rzepaku. Puławy: IUNG; 2003.

[14] Chaudhry AN, Latif MI, Khan AA, Ghulam J, Tanveer I. Comparison of chemical fertilizer with organic manures by using effective microorganisms under maize cropping in rained areas. Int J Biol Biotechnol. 2005;2(4):1001-1006.

[15] Shah SH, Saleem MF, Shahid M. Effect of different fertilizers and effective microorganisms on growth, yield and quality of maize. Int J Agric Biol. 2001;3(4):378-379.

[16] Kaczmarek Z, Wolna-Maruwka A, Jakubus M. Zmiany liczebności wybranych grup drobnoustrojów glebowych oraz aktywności enzymatycznej w glebie inokulowanej efektywnymi mikroorganizmami (EM). J Res Appl Agric Engny Agric Eng. 2008;53(3):118-121.

[17] Bielińska EJ, Baran S, Stankowski S. Ocena przydatności popiołów fluidalnych z węgla kamiennego do celów rolniczych. Inż Roln. 2009;6(115):7-15.

[18] Van Vliet PCJ, Bloem J, de Goede RGM. Microbial diversity, nitrogen loss and grass production after addition of Effective Micro-organisms (EM) to slurry manure. Appl Soil Ecol. www.elsevier.com /locate/apsoil, 2005.

[19] Badura L. Czy znamy wszystkie uwarunkowania funkcji mikroorganizmów w ekosystemach lądowych. Kosmos. 2004;53(3-4):373-379.

[20] Paschoal AD, Homma SK, Jorge MJA, Nogueira MCS. Effect of EM on soil properties and nutrient cycling in a citrus agroecosystem. Third Int Conf Kyusei Nature Farming. Proc Conf Nature Farming for a Sustainable Agriculture. Santa Barbara, California, USA: 1993:284.

[21] Daily MJ, Stewart DPC. Influence of Effective Microorganisms (EM) on vegetable production and carbon mineralization – a preliminary investigation. J Sustain Agricult. 1999;14:15-25.
[22] Freney JR, Melville GE, Williams CH. Organic sulphur fractions labeled by addition of ^{35}S-sulphate to soil. Soil Biol Biochem. 1971;3:133-141.
[23] Goh KM, Gregg PEH. Field studies on the fate of radioactive sulphur fertilizer applied to pasture. Fert Res. 1982;3:337-351.

ZMIANY WYBRANYCH WŁAŚCIWOŚCI GLEBY INKUBOWANEJ Z DODATKIEM AGARU, SKROBI I EFEKTYWNYCH MIKROORGANIZMÓW

[1] Katedra Gleboznawstwa i Ochrony Gruntów,
[2] Katedra Mikrobiologii Ogólnej i Środowiskowej
Uniwersytet Przyrodniczy w Poznaniu

Abstract: Wśród różnych rozwiązań ekologicznych mających zastosowanie w tradycyjnym rolnictwie wskazuje się na dużą przydatność technologii Efektywnych Mikroorganizmów (EM). Preparatowi temu przypisuje się szerokie spektrum działania tak w produkcji roślinnej, jak i zwierzęcej. Wykazuje się, że po zastosowaniu doglebowym omawianego preparatu następuje przyspieszenie procesów mineralizacyjno-humifikacyjnych związków organicznych. Dyskusyjną kwestią są zmiany we właściwościach chemicznych gleb, jakie mogłyby nastąpić w konsekwencji oddziaływania tego kondycjonera.

W związku z powyższym podjęto badania mające na celu określenie wpływu EM na wybrane właściwości fizykochemiczne i chemiczne gleb. Realizacji tego zadania dokonano w oparciu o doświadczenie inkubacyjne z glebą czarna ziemia właściwą zaszczepioną EM, do której dodawano wzrastające dawki agaru lub skrobi.

Uzyskane dane świadczą o różnym wpływie EM z polisacharydami na badane właściwości gleby. W odniesieniu do większości badanych właściwości fizykochemicznych nie stwierdzono oddziaływania istotnego statystycznie. Zmiany ilościowe makro- i mikroskładników były uzależnione od rodzaju polisacharydu oraz jego dawki.

Słowa kluczowe: efektywne mikroorganizmy, agar, skrobia, właściwości fizykochemiczne i chemiczne gleby

DOI: 10.2428/ecea.2012.19(01)007 ECOL CHEM ENG A. 2012;19(1-2):69-76

Andrzej PLAK[1], Piotr BARTMIŃSKI and Ryszard DĘBICKI

SOME REGULARITIES IN ACCUMULATION AND MIGRATION OF HEAVY METALS (Cd, Cu, Pb AND Zn) IN THE SOILS ADJACENT TO STREETS OF LUBLIN

NIEKTÓRE PRAWIDŁOWOŚCI W AKUMULACJI I MIGRACJI METALI CIĘŻKICH (Cd, Cu, Pb I Zn) W GLEBACH SĄSIADUJĄCYCH Z ULICAMI LUBLINA

Abstract: This study attempted to determine the contamination with heavy metals (Cu, Cd, Pb and Zn) of the soils neighbouring on selected streets in Lublin and the effect of the trolley bus line (with uninsulated copper wires). The comparative study was made possible by opening or extensive repair of major traffic routes in Lublin, which was taken into account in selecting the study sites. The total content of copper at the sites ranged from 9.6 to 208.6 mg/kg, lead – from 11.3 to 167 mg/kg, cadmium – from 0.02 to 4.9 mg/kg, and zinc – from 22.9 to 300.6 mg/kg. The portion of bioavailable species in the general pool of heavy metals ranged from 6.7 to 35.3 % for copper, from 7.4 to 36.2 % for lead, from 3.3 to 90.1 % for cadmium, and from 1.7 to 10.7 % for zinc. Soil at the sites situated near the routes with new trolley buses lines contained less common species of the metal as compared with the traffic routes used for several decades. The total content of Cu, Cd, Pb and Zn did not exceed the limit concentrations of heavy metals in class C soils, as laid down in the Regulation of Minister of Environment on the soils and earth quality standards (J. of Laws 02.165.1359 of 04.10.2002).

Keywords: heavy metals, urban soils, traffic pollution

Road transport is a source of considerable contamination with heavy metals of soils adjacent to traffic routes. They come from emission of gas from combustion engines, brake discs, additions of heavy metals to oils, etc. It is particularly important in cities which variable and congested traffic, with a high level of dust in the air and with disturbed air flows. Major pollutants associated with traffic include lead – a component of leaded petrol which was in common use until not long ago. Traffic pollution is more dangerous than that produced by industry because it spreads in relatively high concentrations at low altitudes, in the immediate vicinity of breathing people, animals and plants [1, 2]. Although public transport, including trolley buses, is an environ-

---

[1] Department of Soil Science and Protection, University of Maria Curie-Sklodowska in Lublin, al. Krasnicka 2CD, 20–718 Lublin, Poland, phone: +48 81 537 68 95, email: aplak@poczta.umcs.lublin.pl

mentally-friendly alternative to common use of cars in cities, it is one of the factors which contribute to increased concentration of traffic pollution.

The content of heavy metals (especially lead, copper, zinc and cadmium) in soils may be regarded as an indicator of environmental nuisance of roads [3–5]. Moreover, there is a dense network of trolley bus lines with uninsulated copper wires. In recent years it has been expanded and now covers new residential quarters of the town. Trolley buses do not require special railways because they move among other vehicles; however, the surface layer of electric wires gets rubbed out. Additionally, there is pollution originating from tyre wear and from brake discs.

The aim of the study was to evaluate contamination with Cu, Cd, Pb and Zn of selected traffic routes in Lublin and the effect of trolley bus lines on the content of common and bioavailable species of selected heavy metals in soils in the immediate vicinity of the most busy street of Lublin. The opportunity of conducting the study was provided by opening new trolley bus lines in Lublin, which was taken into account when the study sites were selected. This also made it possible to conduct a comparative study of the soils adjacent to streets where trolley bus lines have existed for several decades with new trolley bus lines and selected traffic routes with no trolley bus lines.

Materials and methods

Eighteen sites were selected for the study, with different characteristics in accordance with the adopted study objectives. Two representative surface soil samples were taken at each site (20–30 cm and 2 m away from the street edge).

The following were determined: pH in 1M KCl – potentiometrically, *total organic carbon* – by the Turin's method, *total exchangeable alkaline cations* as the sum of Ca, Mg, K and Na, extracted from soil with 1 M ammonium acetate and determined by AAS, *hydrolytic acidity* (Hh) by the Kapen's method. Bioavailable forms of Pb, Cu, Cd and Zn were extracted by Lindsey's and Norvell's method; samples were mineralised with *aqua regia* in order to determine total heavy metals; determination was performed by AAS [6, 7].

Results and discussion

Chemical analysis of the soils (Table 1) revealed neutral to alkaline reaction with little variability, ranging from 6.74 to 7.38. Hydrolytic acidity was low and ranged from 0.45 cmol(+)/kg to 1.13 cmol(+)/kg. The soils also had good buffering properties. *Sorptive capacity* (T) varies greatly and ranges from 12.33 to 102.57 cmol(+)/kg. The sorptive complex is almost fully saturated with alkaline cations with calcium cations dominating (Table 1). Such characteristics of total alkaline cations with distinct portion of sodium beside calcium is *a proof of the effect of chemical snow melting agents*.

Surface layers of soil under examination showed varied content of organic carbon (from 8.7 to 45.8 g/kg).

Total copper content in the analysed soils ranged from 9.6 to 208.6 mg/kg, that of lead – from 11.3 to 167 mg/kg, that of cadmium – from 0.02 to 4.9 mg/kg, and that of zinc – from 22.9 to 300.6 mg/kg (Fig. 1). The share of bioavailable species in the total pool of heavy metals ranged from 6.7 to 35.3 % for copper, from 7.4 to 36.2 % for lead, from 3.3 to 90.1 % for cadmium, and from 1.7 to 10.7 % for zinc. Mean total contents of heavy metals (Cu, Cd, Pb, Zn) decreased in the following order Zn > Cu > Pb > Cd, whereas the order was different for mean contents of bioavailable species (Cu > Pb > Zn > Cd).

Table 1

Selected characteristics of analysed soils

Statistical data	pH 1 M KCl	C_{org} [%]	Hh [$cmol^+ \cdot kg^{-1}$]	S [$cmol^+ \cdot kg^{-1}$]	T [$cmol^+ \cdot kg^{-1}$]
min.	6.74	0.52	0.45	11.88	12.33
mean value	7.0	2.54	0.81	31.04	31.85
max	7.38	4.58	1.5	101.97	102.57

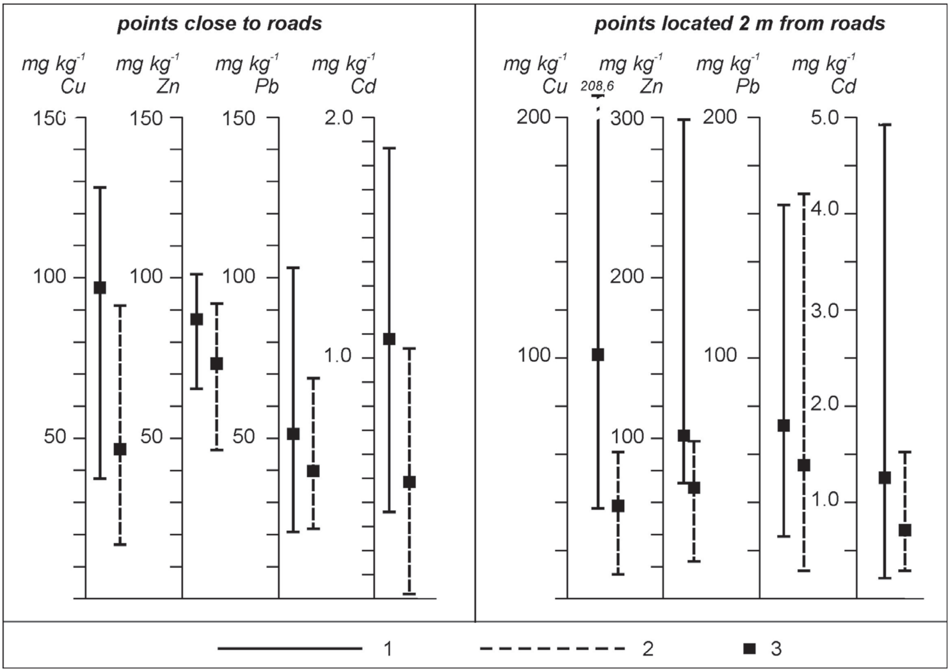

Fig. 1. Total content of selected heavy metals in soils analyzed: 1 – range of concentrations for points with old traction, 2 – range of concentrations for points with new traction, 3 – mean values

Relatively low variability of concentration of *bioavailable species* of the metals at sites situated close to the road edge and 2 m away from it shows that the effect of distance from the source of emission is imperceptible. It is quite *different with common species* of heavy metals, which are distinctly variable. Similarly, as most authors point out, the heavy metal content decreases with increase of the distance from a traffic route [8–10].

The level of contamination of the soils with Cu, Cd, Pb and Zn was assessed based on the limit values, laid down in the Regulation of Minister of Environment on the standards of soil quality and standards of earth quality (J. of Laws 02.165.1359 of 04.10.2002). No limit values for Cu, Pb, Cd or Zn were found to be exceeded in group C soils, which include industrial soils, surface mining land and soils close to traffic routes. The soils under examination contained the metals at amounts which are referred to as acceptable for the soils group. At one site (point 18), a slightly elevated content of copper and lead was recorded.

The experiment results indicate the effect of trolley bus traffic on the total content of copper in the soils neighbouring on the electric line. The soils situated close to the new trolley bus lines contained lower total amounts of the metal. Similar tendencies could be observed by analysing distribution of concentrations of bioavailable species. Soils taken from the study sites situated close to the streets with the newly built trolley bus lines usually contained lower amounts of copper as compared with the sites near the streets where trolley bus lines have existed for several decades.

Moreover, the variable position of the study points show that the effect of traffic on the content of heavy metals in soils near traffic routes is significant [5, 10, 11]. Larger accumulation of the heavy metals under study is usually found in surface samples from the vicinity of routes which have been in use for several decades as compared with the streets which were have been opened or thoroughly repaired within the past several years or months. The average content of common species of heavy metals in the newly opened or thoroughly repaired streets of Lublin were equal to: Cu 35.56 mg/kg, Cd 0.6 mg/kg, Pb 33.55 mg/kg, and Zn 66.98 mg/kg whereas the concentrations in the vicinity of old traffic routes were equal to: Cu 97.29 mg/kg, Cd 1.11 mg/kg, Pb 65.87 mg/kg, and Zn 95.14 mg/kg. Similar regularities were recorded for the species available to plants, which in the soils situated near newly opened or thoroughly repaired roads of Lublin were equal to: Cu 8.6 mg/kg, Cd 0.2 mg/kg, Pb 8.59 mg/kg, and Zn 4.61 mg/kg, whereas near the old traffic routes, the concentrations were equal to Cu 15.71 mg/kg, Cd 0.23 mg/kg, Pb 15.17 mg/kg, and Zn 5.06 mg/kg (Fig. 2).

The statistical analysis of the concentration of heavy metals *vs* variability of organic carbon in the soil under examination reveals statistically significant, strongest correlation with total and bioavailable Cu, somewhat weaker for Pb and Zn, no statistically significant correlation of organic carbon with the content of common species of cadmium and poor correlation in a bioavailable form. Although heavy metals form complexes with humus, which is a way of binding them, the complexes are not particularly stable or dominating.

The statistical analysis did not reveal any significant correlations between total content and the content of bioavailable species of cadmium and zinc and the sorptive capacity of the soils under examination (Table 2). Slightly greater effect on both species were exerted by sorptive capacity T in the case of lead, where primarily bioavailable species showed medium strength correlation. It is difficult to say which component of the sorptive complex has the greatest effect on the content, distribution and mobility of the heavy metals under examination [12].

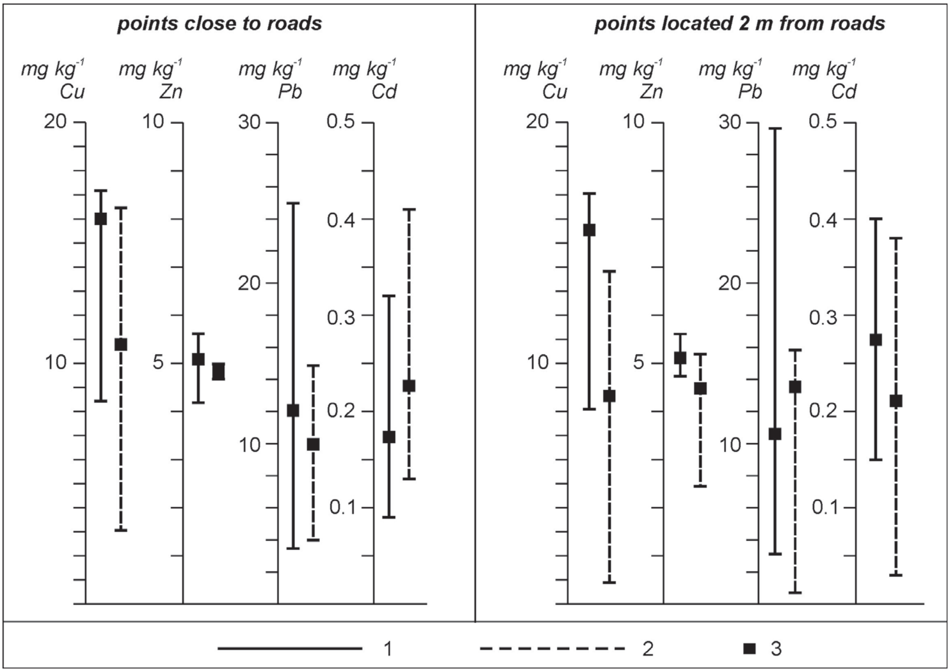

Fig. 2. Content of available form of selected heavy metals in soils analyzed: 1 – range of concentrations for points with old traction, 2 – range of concentrations for points with new traction, 3 – mean values

An analysis of heavy metals concentration in their common and bioavailable species in soils in the immediate vicinity of streets in Lublin *vs* variability of granulometric composition of the soils shows the absence of statistically significant correlations or the presence of only weak ones. Only copper as both species showed medium strength correlation for each of the isolated fractions. Many authors have indicated strong relationships between profile distribution of heavy metals with the smallest fractions; however, no such relationships were shown to exist in the soils in the vicinity of streets in Lublin [13, 14].

Heavy metals undergo various processes in the soil, including accumulation and migration. Metal accumulation depends on various factors, which have been widely discussed in the literature, with the content and nature of organic substances or the content of small grain fractions or the type of land use being dominant [2, 11–13]. The profile distribution of heavy metals in soils in the immediate vicinity of streets depends mainly on the origin of the surface layers which were brought to a site, and on the distance from sources of contamination with heavy metals, *ie* a street. These regularities are valid for young soils which were formed anew as a result of repairs and reconstructions and such soils which have been present close to traffic routes for decades. Current quality of the soils in Lublin, which is expressed as the content of heavy metals (Cd, Cu, Pb, Zn), is affected by origin of the soil layers which have been brought to the site, but also by various anthropogenic factors, the traffic factor being the main one.

Table 2

Chosen correlations between soil parameters (significant at $p < 0.05$)

	pH KCl	pH H_2O	C_{org}	H	Na	K	Mg	Ca	S	T	V	Cu t	Cu dtpa	Zn t	Zn dtpa	Pb t	Pb dtpa	Cd t	Cd dtpa
pH KCl																			
pH H_2O	0.68																		
C_{org}	–0.42																		
H	–0.66	–0.59	0.46																
Na																			
K	–0.51	–0.42	0.42																
Mg																			
Ca			0.46				0.88												
S			0.45				0.89	0.99											
T			0.46				0.89	0.98											
V		0.44		–0.47			0.44	0.65	0.64	0.63									
Cu t			0.5		0.41														
Cu dtpa			0.53		0.41							0.74							
Zn t			0.37									0.7							
Zn dtpa	–0.49		0.4									0.43	0.54						
Pb t			0.43					0.43	0.42	0.42	0.37	0.43	0.38	0.4					
Pb dtpa			0.45					0.49	0.47	0,47	0.44		0.37			0.85			
Cd t																			
Cd dtpa	–0.53		0.35	0.6				0.47	0.47	0.48									

Explanations: H, Na, K, Mg, Ca – exchangeable cations, S – sum of base cations, T – sorptive capacity, V – base saturation, X t – total form of an element, X dtpa – bioavailable form of an element.

Conclusions

1. Total concentration of Cu, Cd, Pb and Zn did not exceed the limit values of concentrations of copper, cadmium, lead or zinc for class C soils, which include industrial areas, surface mining land and traffic areas, laid down in the Regulation of Minister of Environment on the standards of soil quality and standards of earth quality (J. of Laws 02.165.1359 of 04.10.2002), however, the exceeded concentrations of Cu, Pb and Zn of the so called geochemical background show that the area under study is under strong influence of anthropopressure.

2. The proportion of bioavailable species in the total heavy metal pool was varied, which makes it difficult to establish which of the metals under study was the most mobile.

3. The content of common species of heavy metals decreases as the distance from the street edge increases, whereas no significant tendency of this kind was recorded for concentrations of bioavailable species of Cu, Cd, Pb and Zn.

4. Despite being regarded as practically unburdensome to the environment, trolley bus traffic affects the content of common and bioavailable species of copper in the soils adjacent to the electric line. Lower total content of the metal was found at the study sites situated on the routes with new trolley bus lines as compared with the traffic routes which have been in use for decades.

5. Current quality of the soils under study, containing heavy metals (Cd, Cu, Pb, Zn), is affected by the origin of surface layers of soils, which have been brought to the site, but also by a complex of various anthropogenic factors, with the traffic factor dominating.

References

[1] Klimowicz Z, Melke J. Rocz Glebozn. 2000;51(3/4):37-46.

[2] Maciejewska A, Skłodowski P. Zesz Probl Post Nauk Rol. 1995;418(1):271-280.

[3] Niesiobędzka K, Krajewska E. Ochr Środow i Zasob Natural. 2007;31:278-283.

[4] Hanna K, Lassabatere L, Bechet B. J Hazard Mater. 2009;161:1499-1505. 10.1016/j.jhazmat.2008.04.124

[5] Kalembasa D, Pakuła K, Becher M. J Elementol. 2005;10(2):315-324.

[6] ISO 11466: International Standart, Soil quality-extraction of trace elements soluble in aqua regia. First edition, Geneve: 1995.

[7] Lindsay WL, Norvell WA. Soil Sci Soc Amer J. 1978;42:421-435.

[8] Kabata-Pendias A, Pendias H. Biogeochemia pierwiastków śladowych. Warszawa: PWN; 1999.

[9] Olajire AA, Ayodele ET. Environ Int. 1997;23(1):91-101.

[10] Czarnowska K, Bednarz I. Rocz Glebozn. 2000;51(3/4):29-36.

[11] Ma L.Q, Tan F, Harris WG. J Environ Qual. 1997;26:769-775

[12] Sipos P, Nemeth T, Kovacs Kis V, Mohai I. Chemosphere. 2008;73:461-469. 10.1016/j.chemosphere.2008.06.046,

[13] Uziak S, Brogowski Z, Komornicki T. Acta Agrophys. 2005;124:1-157.

[14] Basta NT, Ryan JA, Chaney RL. Environ Qual J. 2005;34:49-63.

NIEKTÓRE PRAWIDŁOWOŚCI W AKUMULACJI I MIGRACJI METALI CIĘŻKICH (Cd, Cu, Pb I Zn) W GLEBACH SĄSIADUJĄCYCH Z ULICAMI LUBLINA

Zakład Gleboznawstwa i Ochrony Gleb, Wydział Nauk o Ziemi i Gospodarki Przestrzennej
Uniwersytet Marii Curie Skłodowskiej w Lublinie

Abstrakt: W pracy została podjęta próba oceny stopnia zanieczyszczenia metalami ciężkimi Cu, Cd, Pb i Zn gleb sąsiadujących z wybranymi ciągami komunikacyjnymi Lublina, oraz wpływu trakcji trolejbusowej (zbudowanej z nieizolowanych drutów miedzianych). Zaplanowane badania porównawcze umożliwił fakt otwarcia, bądź gruntownego remontu ważniejszych arterii komunikacyjnych w Lublinie, co zostało uwzględnione przy wyborze punktów badawczych. Zawartość ogólna miedzi w analizowanych glebach wahała się od 9,6 do 208,6 mg/kg, ołowiu od 11,3 do 167, mg/kg, kadmu od 0,02 do 4,9 mg/kg, a cynku od 22,9 do 300,6 mg/kg. Udział form dostępnych dla roślin w puli ogólnej metali ciężkich stanowił dla miedzi od 6,7 do 35,3%, dla ołowiu od 7,4 do 36,2%, kadmu od 3,3 do 90,1%, a dla cynku 1,7 do 10,7%. Stanowiska zlokalizowane przy trasach z nowymi liniami trolejbusowymi charakteryzowały się mniejszą zawartością ogólną tego pierwiastka, w porównaniu do szlaków komunikacyjnych charakteryzujących się kilkudziesięcioletnim użytkowaniem. Całkowite stężenia Cu, Cd, Pb i Zn nie przekroczyły zawartości granicznych metali ciężkich dla gruntów zaliczanych do grupy C, zamieszczone w Rozporządzeniu Ministra Środowiska w sprawie standardów jakości gleby oraz standardów jakości ziemi (Dz. U. 02.165.1359 z dn. 04.10.2002 r.).

Słowa kluczowe: metale ciężkie, gleby miejskie, zanieczyszczenia komunikacyjne

DOI: 10.2428/ecea.2012.19(01)008 ECOL CHEM ENG A. 2012;19(1-2):77-85

Małgorzata KONCEWICZ-BARAN[1] and Krzysztof GONDEK[1]

ZINC, CADMIUM AND LEAD BINDING BY HUMUS IN SOIL FERTILIZED WITH COMPOSTS

WIĄZANIE CYNKU, KADMU I OŁOWIU PRZEZ PRÓCHNICĘ W GLEBIE NAWOŻONEJ KOMPOSTAMI

Abstract: Binding heavy metals by humus compounds decreases these elements availability to plants, their leaching from soil and causes their partial detoxication. Organic matter supplied to the soil with composts may significantly affect heavy metal availability to plants, therefore the investigations conducted on the basis of a two-year pot experiment aimed at determining the effect of fertilization with composts prepared from plant and other biodegradable wastes and from mixed municipal wastes on zinc, cadmium and lead binding by soil humus. In order to compare the analyzed features, the treatments on which swine manure and nitrogen, phosphorus and potassium in mineral forms were applied, were used. The contents of Zn, Cd and Pb in combination with humus compounds were extracted from the soil by means of 0.025 mol · dm^{-3} NH_4EDTA solution using sequential chemical extraction developed by Zeien and Brümmer. In the obtained extracts the contents of Zn, Cd and Pb were assessed using the ICP-AES method.

Significantly lower acidification was assessed in the soil fertilized with manure and composts than in the soil with a supplement of mineral salts or in unfertilized soil, both after the first and second year of the experiment. Compost fertilization caused an increase in organic carbon content in soil in comparison with organic C assessed in the soil with added mineral salts. The highest total contents of Zn and Pb were determined in the soil with an admixture of municipal waste compost. The contents of lead and zinc bound to humus compounds revealed a positive relationship with organic carbon content and were the highest in the soil receiving organic materials. The biggest contents of cadmium total forms after the first year of the research were assessed in the soil of treatments where the composts and swine manure were used, whereas after the second year contents of Cd in soil did not differ significantly depending on the applied fertilization. An admixture of manure or composts to the soil did not affect significantly the changes of cadmium contents in the combinations with humus compounds.

Keywords: zinc, cadmium, lead, humus, soil, compost

Soil humus compounds may form simple or chelated complex compounds with heavy metal ions. Metal ions may also fulfill the function of bridges in the complexes of humus compounds with clay minerals. Durability of the complexes to a great extend

---

[1] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone: +48 12 662 43 46, fax: +48 12 662 43 41, email: koncewicz_m@wp.pl

depends on the soil pH and the kind of metal ion. Heavy metal binding by humus compounds decreases these elements availability to plants, their leaching into the deeper soil profile layers and causes their partial detoxication [1].

In view of growing organic matter deficit in the soils of Poland, caused by among others diminished amount of applied farmyard manure, alternative sources of organic materials are being sought, which would improve organic matter balance in soil. Composts produced from waste organic materials may provide a valuable and cheap source of organic matter, although one must remember that these materials may be also burdened with undesirable substances, including heavy metals [2–4]. Organic matter supplied to the soil with composts may significantly affect heavy metal availability to plants, therefore the research conducted on the basis of a two-year pot experiment aimed at determining the influence of fertilization with composts prepared from plant and other biodegradable wastes and from mixed municipal wastes on zinc, cadmium and lead binding by soil humus.

Material and methods

The pot experiment, conducted in 2006–2007, comprised 5 treatments in four replications according to the following design: 0 – soil without fertilization, M – soil with mineral salts supplement, SM – soil with swine manure supplement, CI – soil with added compost prepared from plant and other biodegradable wastes, CII – soil with a supplement of mixed municipal waste compost. The experiment was set up on soil with granulometric composition of clay containing 26 % of particles < 0.02 mm in diameter. Selected properties of the soil material were presented in Table 1.

Table 1

Some properties of soil used for the experiment

Determination	Unit	Value
pH KCl	[-]	5.69
Hydrolytic acidity	[mmol(+) · kg^{-1} d.m.]	23.9
Organic C	[g · kg^{-1} d.m.]	15.9
Content of available forms		
P	[mg · kg^{-1} d.m.]	328
K		373
Total content		
Zn	[mg · kg^{-1} d.m.]	104.3
Cd		1.14
Pb		30.2

Two different composts were applied in the experiment: compost from plant and other biodegradable wastes (compost I – CI) originating from the composting plant situated in Krakow-Plaszow, where the wastes are composted using Mut-Kyberferm technology, and compost from mixed municipal wastes (compost II – CII) originating from a composting plant in Katowice operating in Mut-Dano system. The reference materials for the analyzed features in the presented experiment were swine manure and mineral fertilization. Basic chemical properties were assessed in the organic materials using methods developed by Baran and Turski [5]. Chemical composition of organic materials was given in Table 2.

Table 2

Some properties of farmyard manure and composts used in the experiment

Determination	Unit	SM	CI	CII
Dry matter	[g · kg^{-1}]	224.8	475.9	563.4
Organic matter	[g · kg^{-1} d.m.]	823.3	515.8	246.1
pH H_2O	[-]	8.06	7.30	7.18
Electrolytic conductivity	[mS · cm^{-1}]	4.57	3.80	1.41
Total content				
N	[g · kg^{-1} d.m.]	27.31	35.61	6.78
P		13.09	7.17	2.29
K		23.65	25.57	11.16
Ca		2.01	22.57	34.31
Total content				
Zn	[mg · kg^{-1} d.m.]	636.9	282.5	1835.5
Cd		0.61	1.51	6.28
Pb		4.28	14.66	343.67

The swine manure and composts were applied once in the first year of the experiment and their doses were established on the basis of their nitrogen contents. In the first year of the research, nitrogen dose supplied to the soil with the manure and composts was 1.00 g N per pot (8.60 kg of air-dried soil material). Phosphorus and potassium on all treatments (except the unfertilized object) were supplemented to the equal level introduced with the composts and manure, respectively to 0.48 g P · pot^{-1} and 1.64 g K · pot^{-1}. The supplementary phosphorus dose was introduced in a water solution of $Ca(H_2PO_4) \cdot H_2O$ and potassium as a water KCl solution. On the treatment where only mineral salts were used as fertilizers, nitrogen was supplied as NH_4NO_3 while phosphorus and potassium as water solutions of $Ca(H_2PO_4) \cdot H_2O$ and KCl. The quantities of elements supplied to the soil with the swine manure (SM), compost prepared from plant and other biodegradable materials (CI) and compost prepared from mixed municipal wastes (CII) were the following: zinc – 23.31 mg, 7.93 mg and 270.71 mg Zn · pot^{-1}, cadmium: 0.02 mg, 0.04 mg and 0.92 mg Cd · pot^{-1} and lead: 0.15 mg, 0.41 and 50.68 mg Pb · pot^{-1}, respectively. In the second year of the research all treatments, except the unfertilized soil, received supplementary fertilization with nitrogen, phosphorus and potassium applied as water solutions of the following salts: NH_4NO_3, $Ca(H_2PO_4) \cdot H_2O$ and KCl. The amounts of supplied elements were respectively: 0.70 g N, 0.10 g P and 1.60 g K $\cdot$ pot^{-1}.

Each year of the experiment maize, cv. ‘San’ (FAO 240), was cultivated. The maize (designed for green fodder) was always harvested at 7–9 leaves stage. Each year after the crop harvest soil material samples were collected. After drying and grounding in a porcelain mortar the soil material was sifted through a sieve with 1 mm mesh. In the soil samples pH was determined by potentiometer in a suspension of soil and 1 mol $\cdot$ dm^{-3} KCl solution. Organic carbon content was assessed after the sample wet mineralization in potassium dichromate(VI) using Tiurin’s method. Total contents of zinc, cadmium and lead in the soil material were assessed after incineration of the sample organic material in a muffle furnace (at 500 ^{o}C for 8h) and the remains mineralization in concentrated HNO_3 and $HClO_4$ acids (2:1) (v/v). Heavy metal fraction bound to the soil humus compounds (Zn-NH_4EDTA, Cd-NH_4EDTA and Pb-NH_4EDTA) were separated using sequential chemical extraction developed by Zeien and Brümmer [6] by means of 0.025 mol $\cdot$ dm^{-3} NH_4EDTA solution. The contents of zinc, cadmium and lead were assessed in the obtained solutions using ICP-AES method on JY 238 Ultrace apparatus and obtained results were converted into absolutely dry soil mass (105 ^{o}C for 12 h).

The analysis of experimental material was conducted in four replications, whereas the initial materials (organic materials and soil material) in two replications and a plant reference material – NCS DC73348 (China National Analysis Center for Iron & Steel) or soil reference material– *Agro*MAT AG-2 (SCP Science) was added to each analyzed series. The result was considered reliable if the relative standard error did not exceed 5 %.

Two factor ANOVA (factors: fertilization and year) in a completely randomized design using F-Fisher test was conducted for the obtained results. Significance of differences between arithmetic means was estimated on the basis of homogenous groups determined by Duncan test at a significance level $p < 0.05$. Using nonparametric rank Spearman’s test the value of correlation coefficient (r) was computed between organic carbon content in soil and the contents of Zn, Pb and Cd forms in combinations with humus compounds. All statistical calculations were made using Statistica 7.1 pl package.

Results

Fertilization with manure and composts (Table 3) caused a significant increase in the soil pH in comparison with the value assessed in the mineral salts treatment, particularly after the first year of the experiment. The best deacidifying effect was registered after the application of mixed municipal wastes compost (CII).

After two years of the experiment, significantly higher contents of organic carbon were noted in the soil, to which manure or composts were added in comparison with the values assessed in the soil from the treatment where no fertilization was applied or in the soil fertilized only with mineral materials (Table 3).

Table 3

Soil pH and contents of organic carbon in soil assessed after the first and second year of the experiment

Fertilization	pH KCl		Organic C [g · kg^{-1} soil d.m.]	
	1st year	2nd year	1st year	2nd year
0	5.51^{c*}	5.38^{b}	15.21^{a}	14.93^{a}
M	5.40^{b}	5.24^{a}	15.55^{ab}	15.20^{a}
SM	5.59^{e}	5.57^{de}	16.44^{bc}	16.33^{bc}
CI	5.68^{f}	5.53^{cd}	16.26^{bc}	16.22^{bc}
CII	6.29^{g}	6.28^{g}	16.60^{bc}	16.23^{bc}

* Means marked with the same letters do not differ significantly according to Duncan's test at $\alpha < 0.05$; factors: fertilization × year.

In both years of the investigations markedly highest total zinc concentrations were found in the soil with a supplement of compost prepared from municipal wastes (Table 4).

Table 4

Zinc content in soil after the first and second year of the experiment

Fertilization	Total Zn		Zn-NH_4EDTA		Share of Zn-NH_4EDTA in total Zn content [%]	
	[mg · kg^{-1} soil d.m.]					
	1st year	2nd year	1st year	2nd year	1st year	2nd year
0	103.8^{a*}	102.8^{a}	14.90^{a}	14.61^{a}	14.3	14.2
M	106.6^{ab}	104.5^{a}	15.60^{ab}	14.47^{a}	14.6	13.9
SM	108.6^{ab}	107.2^{ab}	16.61^{bc}	16.28^{bc}	15.3	15.2
CI	111.0^{b}	111.1^{b}	17.27^{c}	17.24^{c}	15.6	15.5
CII	126.8^{c}	129.7^{c}	23.34^{d}	22.76^{d}	18.4	17.6

* Means marked with the same letters do not differ significantly according to Duncan's test at $\alpha < 0.05$; factors: fertilization × year.

In the soil of the other treatments the total form of zinc contents did not reveal any significant diversification. The analysis of zinc contents extracted from the soil by means of NH_4EDTA solution after both years of the research revealed the biggest amounts of this Zn form in the soil fertilized with mixed municipal wastes compost (CII), however the share of this zinc form in the total contents did not exceed 18.5 % and on average was by 2.5 % higher than in the soil fertilized with compost based on plant wastes (CI) or manure (SM). Organic carbon content in soil significantly influenced zinc concentrations in combinations with humus compounds ($r = +0.724$; $p < 0.05$).

Significantly highest total lead content after both years of the experiment was assessed in the soil of the treatment where compost prepared from mixed municipal wastes (CII) was used (Table 5). Also the content of lead in combinations with humus compounds was the highest in the soil from compost produced from mixed municipal wastes (CII) treatment. Mean content (for both years) of Pb-NH_4EDTA in this treatment soil was 18.55 mg · kg^{-1} soil d.m., which constituted 55.5 % of this element total soil content. The content of Pb-NH_4EDTA revealed a positive relationship with the soil organic carbon content ($r = +0.538$; $p < 0.05$).

Table 5

Lead content in soil after the first and second year of the experiment

Fertilization	Total Pb		Pb-NH_4EDTA		Share of Pb-NH_4EDTA in total Pb content [%]	
	[mg · kg^{-1} soil d.m.]					
	1st year	2nd year	1st year	2nd year	1st year	2nd year
0	29.30^{b*}	27.92^{ab}	14.17^{ab}	14.20^{ab}	48.4	50.9
M	28.55^{ab}	27.60^{a}	14.12^{ab}	13.95^{a}	49.5	50.5
SM	28.86^{ab}	27.59^{a}	14.71^{bc}	14.28^{abc}	51.0	51.8
CI	29.32^{b}	28.66^{ab}	14.91^{c}	14.49^{abc}	50.9	50.6
CII	33.61^{c}	33.28^{c}	18.93^{e}	18.16^{d}	56.3	54.6

* Means marked with the same letters do not differ significantly according to Duncan's test at $\alpha < 0.05$; factors: fertilization × year.

The highest concentrations of total cadmium after the first year of the experiment were assessed in the soils of compost or manure treatments (Table 6).

Table 6

Cadmium content in soil after the first and second year of the experiment

Fertilization	Total Cd		Cd-NH_4EDTA		Share of Cd-NH_4EDTA in total Cd content [%]	
	[mg · kg^{-1} soil d.m.]					
	1st year	2nd year	1st year	2nd year	1st year	2nd year
0	0.863^{cd}	0.700^{a}	0.347^{bc}	0.273^{a}	40.2	39.0
M	0.813^{bc}	0.701^{a}	0.322^{abc}	0.265^{a}	39.6	37.8
SM	0.900^{cde}	0.744^{ab}	0.298^{ab}	0.290^{ab}	33.1	39.0
CI	0.927^{de}	0.881^{cde}	0.323^{abc}	0.385^{c}	34.8	43.7
CII	0.978^{e}	0.749^{ab}	0.263^{a}	0.282^{ab}	26.9	37.7

* Means marked with the same letters do not differ significantly according to Duncan's test at $\alpha < 0.05$; factors: fertilization × year.

After the second year of the experiment the total cadmium content decreased in the soils of all treatments and generally did not reveal any greater diversification. The content of cadmium bound in organic combinations with the soil humus compounds did not differ significantly either regarding the year of the investigations or applied fertilization. Assessed Cd-NH_4EDTA contents did not reveal any significant relationship with organic carbon concentrations. The highest share of this cadmium fraction in the total content was registered in the soil where compost made of plant and other biodegradable wastes (CI) was applied.

Discussion

Deacidifying effect of the applied composts and manure should be explained by a relatively big load of mainly calcium supplied to the soil with these materials (Table 2). Increasing the soil pH in result of using as fertilizers composts prepared from municipal wastes was observed also by other authors [2, 7].

The increase in soil total concentrations of zinc, cadmium and lead after the application of composts registered in the presented research were also noted by Labetowicz and Ozarowski [2] and by Gorska et al [7] after the application of composts prepared from mixed municipal wastes. Also Izewska et al [8] observed greater concentrations of zinc, lead and cadmium in the soil fertilized with municipal sewage sludge and compost prepared from sewage sludge.

Application of composts for soil fertilization is connected not only with supplying a considerable load of heavy metals but also enriching it in organic matter, which has been demonstrated by numerous investigations [2, 3, 7] and confirmed by the presented results.

Organic matter in mature composts usually shows a considerable ability to bind heavy metals both in the processes of simple ion exchange between the soil solid phase and soil solution, but also through forming coordination compounds [9]. According to Christensen and Christensen [10] and Stroebel et al [11] humic acids may increase bioavailability of heavy metals resulting from the formation of chelates available to plants. Fresh, non-humified organic matter from the ripe or unripe composts provides a source of non-specific humus substances, eg organic acids or polysaccharides forming sparingly soluble complexes with heavy metal ions [12]. Observed in the presented experiment weaker binding of zinc by the soil organic substance in comparison with lead, was also observed by Brazauskiene et al [13] after sewage sludge compost supplying to the soil. The phenomenon should be explained by a greater affinity of humus acids functional groups to lead ions than to zinc ions [14]. According to Baran and Turski [15] humus compounds, beside clay minerals and hydrated iron and aluminium oxides, participate in lead sorption in soil, which is evidently visible in acid soils, where lead bound to organic matter constitutes the main fraction [14].

No significant differences in cadmium fraction bound to humus compounds extracted from the soil fertilized with organic materials or unfertilized or fertilized with mineral salts were observed in the presented investigations. Results of research conducted by Mohamed et al [16] point that introducing organic matter to the soil decreases content of Cd soluble and exchangeable fractions but increases concentrations of fractions bound to humus compounds and residual. The quoted authors explain the transformation of cadmium soluble forms into insoluble ones by among others increasing soil pH and growing contents of organic matter in soil. According to Udom et al [17] increase in organic matter content in soil stimulates formation of durable complexes of humic compounds with cadmium ions and therefore diminishes the share of this element soluble fraction in the total contents.

Conclusions

1. Significantly lower acidification was assessed in the soil fertilized with swine manure and composts than in the soil with mineral salt supplement or in the unfertilized soil.

2. Fertilization with composts increased organic carbon content in soil in comparison with this component content assessed in the soil from the mineral salts treatment.

3. The highest total zinc and lead contents were assessed in the soil with added compost prepared from mixed municipal wastes. The contents of total cadmium forms generally did not differ significantly considering the applied fertilization.

4. The determined contents of lead and zinc in combinations with humus compounds revealed a positive relationship with organic carbon content. A supplement of manure or composts to the soil did not affect significantly the changes of the contents of cadmium bound to humus compounds.

References

[1] Dziadowiec H. Zesz Probl Post Nauk Rol. 1993;411:269-282.
[2] Łabętowicz J., Ożarowski G. Zesz Probl Post Nauk Rol. 2000;472:489-496.
[3] Convertini G, Ferri D, Montemurro F, Maiorana M. Proc. of the 13th Int Soil Conservation Organization Conference, Brisbane: 2004;628:1-4.
[4] Gondek K, Filipek-Mazur B. Acta Agrophys. 2006;8(3):579-590.
[5] Baran S, Turski R. Ćwiczenia specjalistyczne z utylizacji odpadów i ścieków. Wyd AR. Lublin: 1996.
[6] Zeien H, Brümmer GH. Böden Mitteilnng Dtsch Bodenkundl Gesellsch. 1989;59(1):505-510.
[7] Górska EB, Stępień W, Russel S. Zesz Probl Post Nauk Rol. 2007;520:287-293.
[8] Iżewska A, Krzywy E, Wołoszyk Cz. J Elementol. 2009; 14(3):457-466.
[9] Weber J, Karczewska A, Drozd J, Licznar M, Licznar S, Jamroz E, Kocowicz A. Soil Biol Biochem. 2007;39:1294-1302.
[10] Christensen JB, Christensen TH. Environ Sci Technol. 1999;33:3857-3863.
[11] Strobel BW, Borggaard OK, Hansen HCB, Andersen MK, Raulund-Rasmussen K. Eur J Soil Sci. 2005;56:189-196.
[12] Shuman LM. J Environ Qual. 1999;28:1442-1447.
[13] Brazauskiene DN, Paulauskas V, Sabiene N. J Soils Sedim. 2008;8:184-192.
[14] Kabata-Pendias A, Pendias H. Biogeochemia pierwiastków śladowych. Wyd Nauk PWN. Warszawa: 1993.
[15] Baran S, Turski R. Degradacja, ochrona i rekultywacja gleb. Wyd AR. Lublin: 1996.
[16] Mohamed I, Ahamadou B, Li M, Gong M, Cai P, Liang W, Huang Q. J. Soils Sedim. 2010 [online] http://www.springerlink.com/content/j778871238021313/fulltext.pdf
[17] Udom BE, Mbagwu JSC, Adesodun JK, Agbim NN. Environ Int. 2004;30:467-470.

WIĄZANIE CYNKU, KADMU I OŁOWIU PRZEZ PRÓCHNICĘ W GLEBIE NAWOŻONEJ KOMPOSTAMI

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

Abstrakt: Wiązanie metali ciężkich przez związki próchniczne zmniejsza dostępność tych pierwiastków dla roślin, ich wymywanie z gleby oraz powoduje częściową ich detoksykację. Materia organiczna wprowadzona do gleby wraz z kompostami może w znaczący sposób wpływać na dostępność metali ciężkich dla roślin, stąd też celem badań przeprowadzonych w oparciu o dwuletnie doświadczenie wazonowe było określenie wpływu nawożenia kompostami z odpadów roślinnych i innych biodegradowalnych oraz z niesegregowanych odpadów komunalnych na wiązanie cynku, kadmu i ołowiu przez próchnicę glebową. Dla porównania analizowanych cech do schematu doświadczenia wprowadzono obiekty, w których zastosowano obornik od trzody chlewnej oraz azot, fosfor i potas w formie mineralnej. Zawartość Zn, Cd i Pb w połączeniach ze związkami próchnicznymi wyekstrahowano z gleby roztworem NH_4EDTA o stężeniu 0,025 mol · dm^{-3} według sekwencyjnej ekstrakcji chemicznej opracowanej przez Zeiena i Brümmera. W uzyskanych ekstraktach zawartości Zn, Cd i Pb oznaczono metodą ICP-AES na aparacie JY 238 Ultrace.

W glebie nawożonej obornikiem oraz kompostami stwierdzono istotnie mniejsze zakwaszenie niż w glebie z dodatkiem soli mineralnych oraz w glebie nienawożonej zarówno po pierwszym, jak i po drugim roku badań. Nawożenie kompostami spowodowało zwiększenie zawartości węgla organicznego w glebie w porównaniu do zawartości C organicznego oznaczonej w glebie z dodatkiem soli mineralnych. Największe ogólne zawartości Zn i Pb oznaczono w glebie z dodatkiem kompostu z niesegregowanych odpadów komunalnych. Zawartości ołowiu i cynku związane ze związkami próchnicznymi wykazywały dodatnią zależność z zawartością węgla organicznego i były największe w glebie z dodatkiem materiałów organicznych. Największe ogólne zawartości form po pierwszym roku badań oznaczono w glebach z obiektów, w których zastosowano komposty i obornik, zaś po drugim roku zawartość Cd w glebie nie różniła się istotnie ze względu na zastosowane nawożenie. Dodatek do gleby obornika lub kompostów nie powodował istotnych zmian zawartości kadmu w połączeniach ze związkami próchnicznymi.

Słowa kluczowe: cynk, kadm, ołów, próchnica, gleba, kompost

DOI: 10.2428/ecea.2012.19(01)009 ECOL CHEM ENG A. 2012;19(1-2):87-96

Ewa KRZYWY-GAWROŃSKA[1] and Krystyna PRZYBULEWSKA[2]

EVALUATION OF THE DIRECT EFFECT AND AFTER-EFFECT OF ORGANIC FERTILISATION WITHOUT AND WITH PRP SOL ADDITION ON SOIL ENZYMATIC ACTIVITY

OCENA BEZPOŚREDNIEGO I NASTĘPCZEGO DZIAŁANIA NAWOŻENIA ORGANICZNEGO BEZ I Z DODATKIEM PRP SOL NA AKTYWNOŚĆ ENZYMATYCZNĄ GLEBY

Abstract: In a two-year field experiment (2008–2009), the effect of increasing doses of compost being produced with municipal sewage sludge without and with addition of active substance PRP Sol on the activity of urease, dehydrogenase and phosphatases was examined during cultivation of potatoes and spring wheat. The study design included a control object with standard mineral fertilisation and three doses of organic fertilisation. The size of compost doses was determined at a level corresponding to 100, 200 and 300 kg N $\cdot$ ha^{-1}. Organic fertilisation was performed on 28.09.2007. In 2008 and 2009, active substance PRP Sol was introduced into soil in the whole area of experimental field at a dose of 150 kg $\cdot$ ha^{-1} an multicomponent fertiliser Polifoska 6 at a dose of 200 kg $\cdot$ ha^{-1}. Due to low nitrogen content in multicomponent fertiliser Polifoska 6 (6 % N), additional nitrogen fertilisation was applied in the form of urea (46 % N) as the top-dressing at a dose of 80 kg N $\cdot$ ha^{-1} under potatoes and 100 kg N $\cdot$ ha^{-1} under spring wheat at two times. Soil samples for chemical analyses were collected from the arable layer (0–25 cm) from under potatoes (2008) and spring wheat (2009) twice during cultivation of test plants. The carried out study shows that urease activity in soil at soil sample collection times I and II increased on average by 13.2 %, that of phosphatases by 20.2 % and of dehydrogenase by 17.96 % as affected by a single, a doubled and a tripled dose of municipal sewage sludge compost being introduced into soil, whereas in the objects fertilised in addition with PRP Sol respectively by 15.4 %, 35.1 % and 18.65 % when compared with control object without PRP Sol. The applied organic fertilisation with active substance PRP Sol stimulated the enzymatic activity of urease, dehydrogenase and phosphatases in all fertilisation objects when compared with the control one.

Keywords: compost, active substance PRP Sol, soil activity of urease, dehydrogenase and phosphatases

---

[1] Department of Land Reclamation and Environmental Chemistry, Western Pomeranian University of Technology in Szczecin, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, email: ewa.krzywy-gawronska@zut.edu.pl,

[2] Department of Microbiology and Biotechnology of Environment, Western Pomeranian University of Technology in Szczecin, ul. J. Słowackiego 17, 71–434 Szczecin, Poland, email: krystyna.przybulewska@zut.edu.pl

The level of soil enzymatic activity is a sensitive indicator in evaluation of its fertility and capability. Soil enzymatic activity depends to a large extent on optimum moisture and air access to soil, its reaction, heavy metals accumulation, fertilisation, and agrotechnical measures being performed [1–5]. The activity of urease, dehydrogenase, phosphatases and other soil enzymes depends also on soil type, its physicochemical properties as well as on the species of plant being grown on it and its growth and development stage [6–9].

Heavy rise in prices for mineral fertilisers, decreased production of natural fertilisers induced by led to the search for cheaper and environmentally safer sources of nutrients for plants and organic matter for soils.

The manurial value of sewage sludges and composts being produced with them shows that they can be used for soil fertilisation (considerable content of nutrients for plants and organic matter) [10–13]. Attention has been also paid to the possibility of using municipal sewage sludges to produce organic fertilisers which can result in an increase in soil fertility and capability. The application of compost produced with sewage sludge as an organic fertiliser constitutes a valuable source of organic matter. These fertilisers are characterised by a considerable amount of nitrogen and phosphorus, while the content of heavy metals does not exceed the limit values allowing them to be used for environmental and agricultural purposes [14].

Changes in soil environment depend to a greater extent on the activity of respective soil enzymes converted into organic carbon units than on the activity expressed in substrate units per soil mass unit [8]. Results of the studies carried out so far demonstrate that organic and natural fertilisation play a very important part as it determines the carbon content in soil and is in general positively correlated with the activity of enzymes [3, 15, 16].

The studies carried out so far have also shown that active substance PRP Sol contributes, among others, to the improvement of soil physical properties, increases its enzymatic activity and induces the conversion of sparingly available phosphorus, potassium and magnesium forms into compounds which are available for plants [17].

This study aimed at determination of the direct effect and after-effect of organic fertilisation (compost) being applied without and with addition of active substance PRP Sol on the activity of soil enzymes at two soil sample collection times during potato and spring wheat cultivation and after their harvest (2008 and 2009, respectively).

Material and research methods

A field experiment was carried out at the Agricultural Experimental Station in Lipnik belonging to the Western Pomeranian University of Technology in Szczecin. Examinations were performed in 2008 and 2009. The municipal sewage sludge compost being used in examinations was produced by the GWDA method at the Municipal Sewage Treatment Plant in Stargard Szczecinski. It was characterised by neutral reaction (pH_{H_2O} 7.15) and contained decidedly more nitrogen (28.6 $g \cdot kg^{-1}$ d.m.) and phosphorus (12.0 $g \cdot kg^{-1}$ d.m.) when compared to potassium (6.70 $g \cdot kg^{-1}$ d.m.). The total content of heavy metals, which determines the possibility of using it for fertilisation purposes, did not exceed the standards given in the Regulation of the Minister of Agriculture and

Rural Development [18]. The experiment was set up on a field which was characterised by brown, incomplete soil, formed from silty light loamy sand, medium deeply underlaid by sandy loam, of soil quality class IVa and good rye agricultural suitability complex. Soil samples from the field experiment were collected for examinations from the arable layer 0–25 cm. This soil was characterised by a reaction approximating a neutral one (pH_{KCl} 6.65), its organic carbon richness amounted to 7.55, while total nitrogen, phosphorus, potassium, calcium, magnesium and sulphur contents to 0.64, 1.10, 2.41, 2.18, 0.60 and 0.12 $g \cdot kg^{-1}$ d.m., respectively.

The design of field experiment included a control object with standard mineral fertilisation and three doses of organic fertilisation. The size of compost doses was determined at the level corresponding to 100, 200 and 300 $kg\ N \cdot ha^{-1}$. Experiment was conducted without and with addition of active substance PRP Sol. Increasing compost doses were introduced into soil on respective fertilisation objects in autumn 2007. In 2008, test plants were potatoes of the cultivar Ikar, while spring wheat of the cultivar Tybalt in 2009.

In 2008 and 2009, the whole area of experimental field was fertilised with active substance PRP Sol at a dose of 150 $kg \cdot ha^{-1}$ and multicomponent fertiliser Polifoska 6 at a dose of 200 $kg \cdot ha^{-1}$. Due to low nitrogen content in multicomponent fertiliser Polifoska 6 (6 % N), additional nitrogen fertilisation was applied in the form of urea (46 % N) as the topdressing at a dose of 80 $kg\ N \cdot ha^{-1}$ under potatoes and 100 kg $N \cdot ha^{-1}$ under spring wheat at two times. The total dose of nitrogen under spring wheat was divided into two equal parts, applying it at two times (spring – 50 % of this dose before planting or sowing test plants and 50 % of it under spring wheat in the shooting stage or under potatoes during the second ridging).

Soil samples for chemical analyses were collected from the arable layer (0–25 cm) at two times, *ie* twice in 2008 from under potatoes: I – 30 days after planting potato tubers (15.05.2008), and II – after harvesting potato tubers (30.09.2008), while in 2009 spring wheat of the cultivar Tybalt was sown on the same field in spring. Soil samples from under spring wheat were also collected at two times: I – 30 days after sowing (18.04.2009), and II – after harvesting spring wheat (16.08.2009).

Dehydrogenase activity was determined colorometrically with Lambda 150 spectrophotometer at a wavelength of 485 nm after 24-hour incubation at 30 ^{o}C with TTC solution according to the method of Thalman [19]. The activity of urease was determined according to the method of Zantua and Bremner [20], consisting in spectrophotometric measurement of emitted ammonia after soil sample incubation with 2.5 % urease as a substrate at 37 ^{o}C, while that of phosphatases according to the method of Tabatabai [21].

Statistical analysis of the findings was performed using Statistica 8.0 computer software package, whereas differences between mean values were evaluated with the Tukey's test at significance level $p = 0.05$.

Results and discussion

Urease and dehydrogenase activities at two soil sample collection times are compared in Tables 1, 2 and 3. The increasing doses of compost without and with PRP

Sol addition and soil sample collection times in both years of the experiment significantly affected the activity of urease, dehydrogenase and phosphatases.

The findings show that urease activity increased on average by 13.2 %, that of phosphatases by 20.2 % and dehydrogenase activity by 18.0 % as affected by the increasing doses of municipal sewage sludge compost at soil sample collection time I and II, whereas by 15.4 %, 35.1 % and 18.6 %, respectively, in the objects being additionally fertilised with active substance PRP Sol, when compared with control object without PRP Sol addition (Tables 1, 2 and 3).

Factors affecting the variability of enzymatic processes in soil during the vegetation period of test plants are the changing temperature and the amount of atmospheric precipitation [22]. Soil enzymes are decidedly more active at the end of springtime and at the beginning of summer and autumn [23]. Higher dehydrogenase activity was observed in the soil collected in 2009 at soil sample collection times I and II when compared with 2008. The obtained study results are most probably related to air temperature which amounted to 18.7 °C in August 2008 and 19.3 °C in 2009, whereas total atmospheric precipitation was higher in 2009 (75.2 mm) when compared with 2008 (48.8 mm).

Table 1

Effect of soil sample collection time and increasing municipal sewage sludge compost doses and active substance PRP Sol on urease activity. Data are given in mg $\text{N-NH}_4 \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$

Fertilisation variants	Years	Without PRP SOL	With PRP SOL	**Mean**	Without PRP SOL	With PRP SOL	**Mean**
		I times			II times		
I dose of compost	2008 2009	14.1 13.8	14.5 14.0	**14.3** **13.9**	16.2 15.8	16.3 16.1	**16.2** **15.9**
	Mean	**13.9**	**14.0**	**14.1**	**16.0**	**16.2**	**16.1**
II dose of compost	2008 2009	14.0 14.1	14.9 14.4	**14.4** **14.2**	16.4 16.2	16.8 16.5	**16.6** **16.3**
	Mean	**14.0**	**14.6**	**14.3**	**16.3**	**16.6**	**16.4**
II dose of compost	2008 2009	15.1 14.8	15.8 15.2	**15.4** **15.0**	16.5 16.8	16.8 16.4	**16.7** **16.6**
	Mean	**14.9**	**15.5**	**15.2**	**16.6**	**16.6**	**16.6**
$\text{LSD}_{0.05}$							
I – compost doses II – PRP Sol fertilisation I × II		**1.04** **0.13** **1.08**			**0.14** **n.s.** **n.s.**		
Control	2008 2009	13.5 13.6	13.6 13.8	**13.5** **13.7**	13.8 13.5	13.9 14.0	**13.9** **13.7**
	Mean	**13.5**	**13.7**	**13.6**	**13.6**	**13.9**	**13.8**

Urease activity ranged from 13.8 to 16.8 mg $\text{N-NH}_4 \cdot \text{kg}^{-1} \cdot \text{ha}^{-1}$ (Table 1). The soil samples collected in 2008 at soil sample collection time II from under potatoes showed higher urease activity when compared with that determined in the soil samples collected from under spring wheat. The largest increase in urease activity in soil was obtained in 2008 in the object being fertilised with a doubled dose of compost without and with PRP Sol addition between soil sample collection time I and II (May, September), respectively by 17.1 % and 12.7 %. In 2009, an increase in urease activity was observed in the same fertilisation objects but a smaller one, which amounted respectively to 14.9 % and 14.58 %. The lowest urease activity was observed in the objects fertilised with a single dose of compost itself. Highly significant increase in the activity of enzyme being discussed was observed in the objects with a doubled and a tripled dose of compost without and with PRP Sol addition when compared with control object. Significant increase in urease activity in the soil being fertilised with sewage sludge or compost produced with it is confirmed by studies of other authors [24]. Soil sample collection time had a significant effect on increase in urease activity. Respective fertilisation objects were characterised by different activity levels in relation to control object. Such a differentiation in the activity of urease, *ie* of an enzyme catalysing urea decomposition, may be evidence of various mineralisation rate of nitrogen compounds in the soil samples under examination [25].

When comparing the activity of urease in soil samples, significantly larger effect of organic fertilisation without and with PRP Sol addition on the activity of enzyme being examined in the soil samples collected from under potatoes (2008) was shown when compared with the soil material collected from under spring wheat (2009).

Differences in urease activity between soil sample collection times probably result from the protective effect of mineral and organic colloids in relation to urease, producing complex compounds with them [26]. This is evidenced by more intense activity of urease in the soil with higher sorptive capacity and its positive response to compost fertilisation. Urease is strongly immobilised by organic matter but larger stability of that enzyme is ensured by composted organic mass than the fresh one [26]. Perhaps differences in urease stimulation by compost should be seen in the degree of compost organic matter decomposition. After two years of experiment, average urease activity in the soil fertilised solely with increasing compost doses amounted to 15.3 mg $N\text{-}NH_4 \cdot kg^{-1} \cdot h^{-1}$ and was higher by 1.75 unit when compared with control object (Table 1).

Dehydrogenase activity ranged from 13.1 to 16.4 cm $\cdot$ $H_2 \cdot kg^{-1} \cdot d^{-1}$. The soil samples collected in 2009 from under spring wheat showed higher dehydrogenase activity when compared with that being determined in the soil samples collected from under potatoes (2008); see Table 2.

Dehydrogenase activity in the soil samples collected in 2009 between soil sample collection time I and II (April, August) increased respectively by 3.03 % and 10.03 % as affected by the increasing doses of compost without and with PRP Sol addition being introduced into soil. On the other hand, an increase in dehydrogenase activity in 2008 in the same fertilisation objects was smaller and amounted respectively to 1.95 % and 9.00 %. The highest dehydrogenase activity in the soil samples collected from under spring wheat (2009) was characteristic of the object being fertilised with a doubled and a tripled dose of compost with PRP Sol addition, between soil sample collection time I

Table 2

Effect of soil sample collection time and increasing municipal sewage sludge compost doses and active substance PRP Sol on dehydrogenase activity. Data are given in $\text{cm} \cdot \text{H}_2 \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$

Fertilisation variants	Years	Without PRP SOL	With PRP SOL	**Mean**	Without PRP SOL	With PRP SOL	**Mean**
		I times			II times		
I dose of compost	**2008** **2009**	13.4 13.6	13.1 13.8	**13.2** **13.7**	13.7 14.1	14.2 14.6	**13.8** **14.3**
	Mean	**13.5**	**13.4**	**13.4**	**13.8**	**13.8**	**13.8**
II dose of compost	**2008** **2009**	14.2 14.5	13.9 14.3	**14.0** **14.4**	14.4 15.0	15.1 15.4	**14.7** **15.2**
	Mean	**14.3**	**14.1**	**14.2**	**14.7**	**15.2**	**15.0**
III dose of compost	**2008** **2009**	14.6 14.9	14.1 14.1	**14.3** **14.5**	14.9 15.1	15.5 16.4	**15.2** **15.7**
	Mean	**14.7**	**14.1**	**14.4**	**15.0**	**15.9**	**15.5**
$\text{LSD}_{(0.05)}$							
I – compost doses	**1.26**				**1.18**		
II – PRP Sol fertilisation	**n.s.**				**0.42**		
I × II	**n.s.**				**n.s.**		
Control	2008 2009	12.1 12.0	12.6 12.4	**12.3** **12.2**	12.2 12.3	12.8 12.7	**12.5** **12.5**
	Mean	**12.1**	**12.5**	**12.3**	**12.2**	**12.8**	**12.5**

and II (April, August). Dehydrogenase activity in these fertilisation objects and between soil sample collection time increased respectively by 7.69 % and 16.3 %. Smaller increase in dehydrogenase activity, respectively by 3.67 % and 3.45 %, was obtained in the objects with a doubled and a tripled dose of compost itself being introduced into soil (Table 2). The applied fertilisation with a doubled and a tripled dose of compost with PRP Sol addition between soil sample collection time I and II contributed to an increase in dehydrogenase activity, respectively by 7.80 % and 12.8 %.

Dehydrogenase activity in the soil samples collected from under spring wheat (2009) was significantly higher as affected by fertilisation with the increasing doses of compost with PRP Sol addition when compared with control object. Active substance PRP Sol being introduced into soil significantly induced an increase in the enzyme under discussion in the soil material collected in 2008 and 2009.

The activity of phosphatases in the first study year (2008) was in the range of 1.11 to 1.86 mmol PNP $\cdot$ $\text{kg}^{-1} \cdot \text{h}^{-1}$, whereas in the second one (2009) ranged from 1.20 to 1.79 mmol PNP $\cdot$ $\text{kg}^{-1} \cdot \text{h}^{-1}$ (Table 3). The soil of control object was characterised, on average of two years, by the lowest activity of that enzyme. In the soil samples collected in 2009 at soil sample collection time I (April), higher activity of phosphatases was observed when compared to 2008 (May) in the objects with a single, a doubled and a tripled dose of compost without and with PRP Sol addition, which increased on average by 6.03 %, 5.42. % and 4.89 %, respectively. On the other hand, in the soil samples collected at soil sample collection time II after harvesting test plants (September 2008, August 2009), this correlation was opposite. Higher activity of phosphatases in all fertilisation objects was characteristic of the soil collected at soil sample collection time II in 2008 when compared to soil sample collection time II in 2009 (Table 3).

Table 3

Effect of soil sample collection time and increasing municipal sewage sludge compost doses and active substance PRP Sol on the activity of phosphatases.
Data are given in mmol PNP $\cdot$ kg^{-1} $\cdot$ h^{-1}.

Fertilisation variants	Yares	Without PRP SOL	With PRP SOL	**Mean**	Without PRP SOL	With PRP SOL	**Mean**
		I times			II times		
I dose of compost	2008	1.11	1.22	**1.16**	1.36	1.56	**1.46**
	2009	1.20	1.26	**1.23**	1.31	1.47	**1.39**
Mean		**1.15**	**1.24**	**1.19**	**1.33**	**1.51**	**1.42**
II dose of compost	2008	1.21	1.36	**1.29**	1.48	1.69	**1.58**
	2009	1.31	1.42	**1.36**	1.40	1.65	**1.53**
Mean		**1.26**	**1.39**	**1.32**	**1.44**	**1.67**	**1.55**
III dose of compost	2008	1.38	1.48	**1.43**	1.60	1.86	**1.73**
	2009	1.41	1.59	**1.50**	1.57	1.79	**1.68**
Mean		**1.39**	**1.53**	**1.46**	**1.58**	**1.82**	**1.70**
LSD$_{0.05}$							
I – compost doses		**0.13**			**0.100**		
II – PRP Sol fertilisation		**0.04**			**0.045**		
I × II		**n.s.**			**n.s.**		
Control	2008	1.04	1.10	**1.07**	1.20	1.34	**1.27**
	2009	1.06	1.09	**1.07**	1.22	1.30	**1.26**
Mean		**1.05**	**1.09**	**1.07**	**1.21**	**1.32**	**1.26**

The applied fertilisation with a doubled and a tripled dose of compost with PRP Sol addition between soil sample collection time I and II contributed to an increase in the activity of phosphatases by 24.3 % and 25.7 %, respectively. Smaller increase in the activity of enzyme under discussion was obtained in the object with a single dose of compost with PRP Sol addition being introduced into soil, which amounted to 16.7 %.

Introduction of exclusive fertilisation with municipal sewage sludge compost significantly affected increase in the enzymatic activity of phosphatases between doses of that organic fertiliser. Average increase in the activity of phosphatases between dose I and III, II and III, and I and II amounted respectively to 20.8 %, 10.3 % and 9.60 %. Addition of active substance PRP Sol at a dose of 150 kg $\cdot$ ha^{-1} to increasing compost doses contributed to significant increase in the activity of that enzyme in the analysed soil. Increase in the activity of dehydrogenase and phosphatases in the soil where fertilisation with municipal sewage sludge compost was applied is confirmed by other studies [27]. Many authors indicate higher enzymatic activity in soils with large sorptive capacity and larger moisture [28].

When analysing the period of two study years, average increase in the activity of phosphatases was observed between sample collection time I and II in the objects with a single, a doubled and a tripled dose of compost itself being introduced into soil, respectively by 15.6 %, 14.3 % and 13.7 %, while in the objects with compost and PRP Sol by 21.8 %, 20.1 % and 18.9 %.

Significant effect on increase in the enzymatic activity of phosphatases had organic fertilisation without and with PRP Sol addition and soil sample collection times.

Conclusions

1. Fertilisation with municipal sewage sludge compost without and with PRP Sol addition stimulates the activity of urease, dehydrogenase and phosphatases in soil. Their effect depends on the size of compost dose introduced into soil and soil sample collection time.
2. The largest increase in urease activity in soil was obtained in 2009 in the objects being fertilised with a doubled dose of compost without and with PRP Sol addition between soil sample collection time I and II.
3. The carried out study shows that urease activity in soil at soil sample collection times I and II increased on average by 13.2 %, that of phosphatases by 20.2 % and of dehydrogenase by 17.96 % as affected by a single, a doubled and a tripled dose of municipal sewage sludge compost being introduced into soil, whereas in the objects fertilised in addition with PRP Sol respectively by 15.4 %, 35.1 % and 18.65 % when compared with control object without PRP Sol.
4. Higher activity of the enzymes under examination was observed in the objects fertilised with municipal sewage sludge compost and PRP Sol addition when compared with those fertilised solely with compost.
5. The applied fertilisation with increasing doses of municipal sewage sludge compost without and with PRP Sol addition increases the activity of urease, dehydrogenase and phosphatases when compared with control object.

References

[1] Cieśla W, Koper J. Wpływ wielokrotnego nawożenia mineralno-organicznego na kształtowanie się poziomu fosforu organicznego i przyswajalnego oraz aktywność enzymatyczną gleby. Rocz Gleboz. 1990;41:73-83.

[2] Wyszkowska J, Kucharski J. Nawożenie słomą i trocinami jako czynnik niwelujący oddziaływanie zanieczyszczenia gleby kadmem na drobnoustroje. Zesz Probl Post Nauk Rol. 2005;506:557-568.

[3] Zhao Y, Wang P, Li J, Chen Y, Ying X, Liu S. The effect of two organic manures on soil properties and crop yields on a temperate calcareous soil under a wheat-maize cropping system. Europ J Agron. 2009;31(1):36-42. DOI:10.1016/j.eja.2009.03.001.

[4] Bielińska EJ, Baran S, Domżał H. Zastosowanie wskaźników enzymatycznych do oceny wpływu rocznych zabiegów agrotechnicznych na poprawę właściwości gleby lekkiej. Folia Univ Agric Stetin Ser Agriculturae. 2000;211(84):35-40.

[5] Bielińska EJ, Żukowska G. Aktywność proteazy i ureazy w glebie lekkiej użyźnionej osadem ściekowym. Acta Agrophys. 2002;70:41-47.

[6] Renella G, Landi L, Valori F, Nannipieri P. Microbial and hydrolase activity after relase of low molecular weight organic compounds by a model root surface in a clayey and a sand soil. Appl Soil Ecol. 2007;36:124-129.

[7] Nortcliff S. Standarisation of soil quality attributes. Agric Ecosys Environ. 2002;88:161-168.

[8] Trasar-Cepeda C, Leiros MC, Gil-Sotres F. Hydrolytic enzyme activities in agricultural and forest soils. Some implications for their use a indicators of soil quality. Soil Biol Biochem. 2008;40:2146-2155.

[9] Yang L, Li T, Li F, Lemcoff JH, Cohen S. Fertilization regulates soil enzymatic activity and ferility dynamics in cucumber field. Scientia Horticul. 2008;116:21-26.

[10] Baran S. Zasoby i gospodarka odpadami organicznymi w Polsce. Wybrane aspekty zagospodarowania odpadów organicznych a produkcja biomasy wierzby energetycznej. Wyd URzeszów. 2005;17-40.

[11] Krzywy E, Krzywy J. Optymalizacja właściwości nawozowych odpadów pochodzenia organicznego w wyniku ich kompostowania. Wybrane aspekty zagospodarowania odpadów organicznych a produkcja biomasy wierzby energetycznej. Wyd Rzeszów. 2005;41-62

[12] Urbaniak M. Przeróbka i wykorzystanie osadów ze ścieków komunalnych. Łódź: Wydaw. PAN; 1997.

[13] Wołoszyk Cz. Agrochemiczna ocena nawożenia kompostami z komunalnych osadów ściekowych i odpadów przemysłowych. Rozprawa habilitacyjna 217. Wyd AR w Szczecinie, Szczecin: 2003.

[14] Baran S, Wójcikowska-Kapusta A, Żukowska G. Ocena przydatności osadu ściekowego i wełny mineralnej Grodan do rekultywacji gruntu bezglebowego na podstawie zawartości przyswajalnych form fosforu, potasu i magnezu. Rocz. Glebozn. 2006;LVII 1/2:21-31.

[15] Saha S, Prakash V, Kundu S, Kumar N, Mina BL. Soil enzymatic activity as affected by long term application of farm yard manure and mineral fertilizer under a rainfed soybean–wheat system in N-W Himalaya. Europ J Soil Biol. 2008;44:309-315

[16] Venkatesan S, Senthurpandian VK. Comparision od enzyme activity with depth under tee plantations and forested sites in south India. Geoderma. 2006;137:212-216.

[17] Krzywy-Gawrońska E. Badania wpływu kompostu z komunalnego osadu ściekowego i substancji czynnej PRP Sol na żyzność i urodzajność gleby. Wyd ZUT w Szczecinie; 2009.

[18] Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi z dnia 18 czerwca 2008 r. w sprawie wykonywania niektórych przepisów ustawy o nawozach i nawożeniu. DzU z dnia 2 lipca 2008 r., nr 119, poz. 765.

[19] Thalmann A. Zur Methodik derestimmung der Dehydrogenase aktivit in Boden mittels. Triphenyltetrazoliumchlorid (TTC). Landwirtsch. Forsch. 1969;21:249-258.

[20] Zantua MI, Bremner JM. Comparison of methods of assaying urease activity in soils. Soil Biol Biochem. 1975;7:291-295.

[21] Tabatabai MA, Bremner JM. Use of p-nitrophenyl phosphate for assay of soil phosphatase activity. Soil Biol Biochem. 1974;1:301-307.

[22] Gianfred AL, Ruggiero P. Enzyme activities in soil. W.P. Nannipieri, K. Smalla (ed.): Soil biology. Nucleic acids and proteins in soil. Springer-Verlang 2006;8:257-311.

[23] Januszek K. Seasonal changes of enzyme activity in mor, moder and mull humus of selected forest soils in the Western Beskid Mountains. Fol For Pol. 1993;35:59-75.

[24] Kuziemska B, Kalembasa S. Wpływ wapnowania, nawożenia organicznego oraz zanieczyszczenia gleby niklem na aktywność ureazy, zawartość węgla i azotu w glebie po kolejnych zbiorach kupkówki pospolitej. Zesz Probl Post Nauk Rol. 2008;533:259-267.

[25] Sołek-Podwika K, Ciarkowska K. Aktywność ureazy w glebach antropogenicznie wzbogaconych w związki siarki. Rocz Glebozn. 2008;LIX 2:196-200.

[26] Pascual JA, Moreno JL, Harandez T, Garcia C. Persistence of immobiliser and Total urease and phosphatase in a soil amened with organic wastes. Biores Technol. 2002;82:73-78.

[27] Krzywy J, Joniak K, Krzywy E, Krzywy-Gawrońska E.: Wpływ kompostów i nawozów mineralnych na aktywność dehydrogenazy, fosfatazy kwasnej i zasadowej oraz ureazy w glebie przed siewem i po zbiorze rzepaku jarego. Zesz Probl. Post Nauk Roln. 2006;512:381-389.

[28] Bielińska J, Tomaszewicz T. Wpływ czynników antropogenicznych na aktywność enzymatyczną gleb poboczy dróg. Rocz Glebozn. 2006;LVII 1/2:50-58.

OCENA BEZPOŚREDNIEGO I NASTĘPCZEGO DZIAŁANIA NAWOŻENIA ORGANICZNEGO BEZ I Z DODATKIEM PRP SOL NA AKTYWNOŚĆ ENZYMATYCZNĄ GLEBY

[1] Zakład Rekultywacji i Chemii Środowiska,
[2] Zakład Mikrobiologii i Biotechnologii Środowiska
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

Abstrakt: W dwuletnim doświadczeniu polowym (2008–2009) badano wpływ wzrastających dawek kompostu wyprodukowanego z komunalnego osadu ściekowego bez i z dodatkiem substancji czynnej PRP Sol na aktywność ureazy, dehydrogenazy i fosfataz w trakcie uprawy ziemniaka i pszenicy jarej. Schemat badań obejmował obiekt kontrolny ze standardowym nawożeniem mineralnym oraz trzy dawki nawożenia organicznego. Ilość dawek kompostu ustalono na poziomie odpowiadającym 100, 200 i 300 kg N · ha^{-1}. Nawożenie organiczne wykonano 28.09.2007 r. W latach 2008 i 2009 na całą powierzchnię doświadczenia wprowadzono substancją czynną PRP Sol w dawce 150 kg · ha^{-1} oraz Polifoskę 6 w dawce 200 kg · ha^{-1}. Ze względu na niewielką zawartość azotu w Polifosce 6 (6 % N) zastosowano pogłównie mocznik w dawce odpowiadającej 100 kg N · ha^{-1} pod ziemniaka i pszenicę jarą w dwóch terminach. Próbki glebowe do analiz chemicznych pobrano z warstwy ornej (0–25 cm) spod ziemniaka (2008 r.) i pszenicy jarej (2009 r.) dwukrotnie w okresie uprawy roślin testowych. Z przeprowadzonych badań wynika, że pod wpływem wprowadzonej pojedynczej, podwojonej i potrojonej dawki kompostu z udziałem komunalnego osadu ściekowego w I i II terminie pobierania próbek glebowych średnio w glebie zwiększyła się aktywność ureazy o 13,2 %, fosfataz o 20,2 % i dehydrogenazy o 18,0 %, natomiast na obiektach nawożonych dodatkowo PRP Sol odpowiednio o 15,4 %, 35,1 % i 18,6 % w porównaniu z obiektem kontrolnym bez PRP Sol. Zastosowane nawożenie organiczne łącznie z substancją PRP Sol stymulowało aktywność enzymatyczną ureazy, dehydrogenazy i fosfataz na wszystkich obiektach nawozowych w porównaniu do obiektu kontrolnego.

Słowa kluczowe: kompost, substancja czynna PRP Sol, aktywność w glebie ureazy, dehydrogenazy i fosfataz

DOI: 10.2428/ecea.2012.19(01)010 ECOL CHEM ENG A. 2012;19(1-2):97-104

Krzysztof KUD[1] and Leszek WOŹNIAK[2]

SELECTED TRACE ELEMENTS IN SOIL AND PLANTS FROM MARSHY MEADOWS OF THE SAN RIVER VALLEY

WYBRANE MIKROELEMENTY W GLEBACH I ROŚLINACH ŁĄK ŁĘGOWYCH DOLINY SANU

Abstract: The research was conducted out on meadows located on floodplain terrains in the San River valley. The subject of the study was Ni, Mn and Co content in soils and plants marshy ecosystems. The total content of analyzed elements and the contents their soluble forms in 1 mol HCl $\cdot$ dm^{-3} were estimated in collected soils.

Alluvial soils and turf layer were characterized by natural content of these elements. Fresh alluvial were rich in $CaCO_3$ and other studied elements.

Keywords: alluvial soils, fresh alluvial, nickel, manganese, cobalt, the San River valley

Terrains of marshy meadows are extremely valuable ecosystems which depend on seasonal floods. Green grasslands localized on marshy meadows of the San River valley were subjects of presented studies. There were described selected trace elements in ecosystems of grasslands located in alluvial soils of the San River valley.

Material and methods

The researches were conducted in all the San River valley. Soil samples were picked up from grasslands at two layers – ie at 0–10 cm and 10–30 cm depth. From the places where the soil was picked up there were prior removed meadows sward and the fresh alluvial were collected after floods run away. The collected soil material was analyzed according to the commonly used methods using in agrochemical laboratories [1]. In order to analyze Ni, Mn and Co content the soil samples were mineralized in $HClO_4$, the

---

[1] Department of Enterprise, Management and Ecoinnovation, Faculty of Management, Rzeszow University of Technology, al. Powstańców Warszawy 8, 35–959 Rzeszów, Poland, phone: +48 17 865 11 65, email: kkud@prz.edu.pl

[2] Department of Enterprise, Management and Ecoinnovation, Faculty of Management, Rzeszow University of Technology, al. Powstańców Warszawy 8, 35–959 Rzeszów, Poland, phone: +48 17 865 11 65, email: lwozniak@prz.edu.pl

determination was made by means of atomic absorption spectrophotometry. Because of low Ni and Co concentration in basic solution these two elements were condensed in organic phase. The total contents of analyzed elements and the contents of their soluble forms in 1 mol HCl $\cdot$ dm^{-3} were estimated in studied soils.

After drying to absolutely dry mass, the plant material was mineralized in mixture of acids – HNO_3, $HClO_4$ and H_2SO_4 in proportion 20 : 5 : 1. The content of Ni, Mn and Co was also determined in soil material.

The samples were collected at the same time when the first crop of the grass is harvested. The contents of Ni, Mn and Co in fresh alluvial, plants and soils in the San River valley was the purpose of researches. In researches it decide to demonstrate the argument that the fresh alluvial have positive influence on meadows soils.

Results

The basic characteristics of alluvial soils from the San River valley were presented in Table 1.

Table 1

The basic parameters of fresh alluvial and studied alluvial soils from the San River valley

Parameter	Arithmetic mean	Geometric mean	Median	Scope	
				Minimum	Maximum
			Fresh alluvial (n = 53)		
Granulometric composition [%]					
Particles diameter:					
1.0–0.1 mm	45.40	36.08	44	2	98
0.1–0.02 mm	32.66	27.20	33	1	56
< 0.02 mm	21.94	16.51	20	1	67
< 0.002 mm	4.53	3.48	4	1	18
pH in H_2O	7.47	7.53	7.51	7.09	8.21
pH in KCl	7.17	7.25	7.24	6.66	7.99
$CaCO_3$ [g $\cdot$ kg^{-1} d.m.]	49.21	42.03	52.62	9.37	98.24
C_{org} [g $\cdot$ kg^{-1} d.m.]	18.4	14.0	19.0	0.42	79.8
			Layer 0–10 cm (n = 48)		
Granulometric composition [%]					
Particles diameter:					
1.0–0.1 mm	28.9	24.2	26.0	4	80
0.1–0.02 mm	38.7	37.1	37.5	13	57
< 0.02 mm	32.4	28.4	30.5	7	73
< 0.002 mm	8.3	6.3	7.0	1	21
pH in H_2O	6.63	7.14	7.36	5.50	7.91
pH in KCl	5.22	6.21	6.55	3.88	7.07
$CaCO_3$ [g $\cdot$ kg^{-1} d.m.]	20.86	12.83	13.98	0.80	72.99
C_{org} [g $\cdot$ kg^{-1} d.m.]	19.7	17.6	19.4	1.2	54.0

Table 1 cont.

Parameter	Arithmetic mean	Geometric mean	Median	Scope	
				Minimum	Maximum
Layer 10–30 cm (n = 48)					
Granulometric composition [%]					
Particles diameter:					
1.0–0.1 mm	24.6	20.9	22.0	5	52
0.1–0.02 mm	39.8	38.8	40.5	24	58
< 0.02 mm	35.6	32.8	33.5	13	68
< 0.002 mm	10.5	9.0	8.5	2	22
pH in H_2O	6.68	7.34	7.65	5.54	8.10
pH in KCl	5.33	6.30	6.65	4.21	7.07
$CaCO_3$ [$g \cdot kg^{-1}$ d.m.]	22.14	14.29	16.92	0.80	57.71
C_{org} [$g \cdot kg^{-1}$ d.m.]	11.3	9.3	11.2	0.5	19.6

The studied soils possessed generally neutral or alkaline reaction. Fresh alluvial were rich in $CaCO_3$, geometric mean equaled 42.03 $g \cdot kg^{-1}$ of d.m.

In places where floods appeared the deposited carbonate of calcium prevented soil acidification. In situations when floodbanks cut-off the floods the soil profiles have gradually acidified themselves and there have started the process of transformation from alluvial soils into brown alluvial soils.

In Table 2 there were presented: a range, median, arithmetic and geometric mean for Ni, Mn and Co in alluvial soils, fresh alluvial and grassland vegetation.

Table 2

Content of studied elements [$mg \cdot kg^{-1}$] in alluvial soils, grassland vegetation and fresh alluvial from the San River valley

Metal content	Arithmetic mean	Geometric mean	Median	Scope	
				Minimum	Maximum
Alluvial soils, layer 0–10 cm (n = 48)					
Total Ni	31.05	29.56	30.04	11.18	54.76
Soluble Ni	7.69	6.87	7.85	1.40	15.30
Total Mn	617.0	584.0	575.0	256.0	1166.0
Soluble Mn	463.0	427.0	429.0	151.0	995.0
Total Co	8.34	7.84	7.95	3.30	17.20
Soluble Co	3.22	3.00	3.10	0.90	5.60
Alluvial soils, layer 10–30 cm (n = 48)					
Total Ni	30.77	29.66	28.92	17.78	50.40
Soluble Ni	7.56	6.54	8.05	0.30	19.40
Total Mn	611.0	580.0	564.0	261.0	1059.0
Soluble Mn	416.0	375.0	391.0	104.0	901.0
Total Co	8.54	8.10	7.92	5.00	17.81
Soluble Co	3.00	2.75	2.90	0.80	5.10

Table 2 cont.

Metal content	Arithmetic mean	Geometric mean	Median	Scope	
				Minimum	Maximum
Grassland vegetation (n = 48)					
Ni	1.31	1.17	1.20	0.39	3.71
Mn	58.31	46.82	43.50	16.80	228.80
Co	0.13	0.09	0.09	0.02	0.52
Fresh alluvial (n = 53)					
Total Ni	23.69	21.24	22.52	5.90	45.69
Soluble Ni	6.00	4.68	6.20	0.10	12.80
Total Mn	752.7	623.6	554.0	270.0	3437.0
Soluble Mn	637.2	514.6	450.0	188.0	2284.0
Total Co	6.62	6.04	5.73	1.88	12.31
Soluble Co	2.57	2.22	2.40	0.30	5.20

In Figures from 1 to 5 there were presented the studied elements in a range of: 25 % – lower quartile, 50 % median and 75 % upper quartile.

Mean content of total Ni in turf and under-turf layer of alluvial soils from the San River valley was very similar (Table 2). However there was observed a less interquartile range and variability (Fig. 1).

Content of soluble in 1 mol HCl · dm^{-3} forms of Ni did not revealed any differences between studied layers; a broader range was visible in deeper layer.

Nickel content in grassland vegetation ranged in 0.39–3.71 mg · kg^{-1} d.m. It is worth to add that lower quartile was 0.83 and upper one 1.59 mg · kg^{-1} d.m. (Fig. 1).

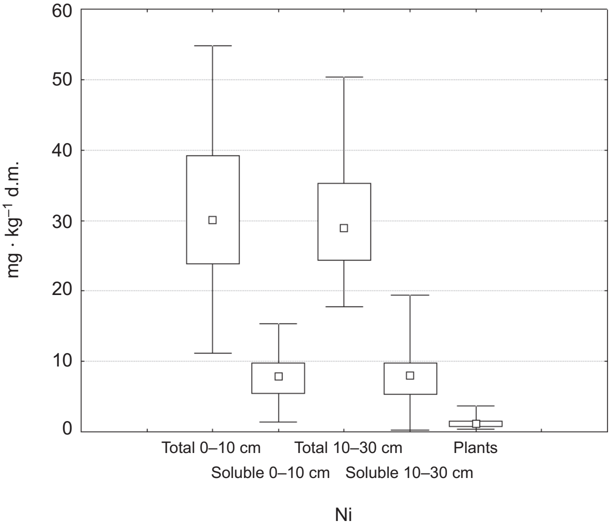

Fig. 1. Nickel content in alluvial soils in 0–10 cm and 10–30 cm layer and in plants

Manganese content was similar in both layers of studied soils ie total and soluble forms of this element (Fig. 2).

The Mn content in grassland vegetation ranged from 16.8 to 228.8 mg · kg^{-1} d.m. (Table 2), however in Fig. 2 there was presented a range between quartiles which was 29.0–71.45 mg · kg^{-1} d.m., it means that 75 % of observations were not over 72 mg · kg^{-1} d.m.

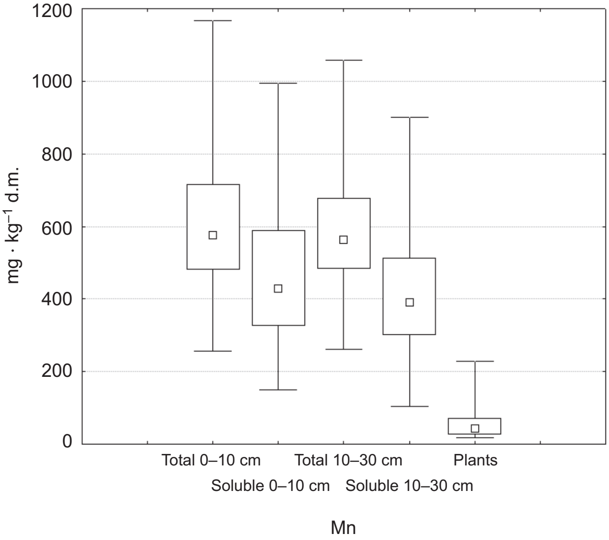

Fig. 2. Manganese content in alluvial soils in 0–10 cm and 10–30 cm layer and in plants

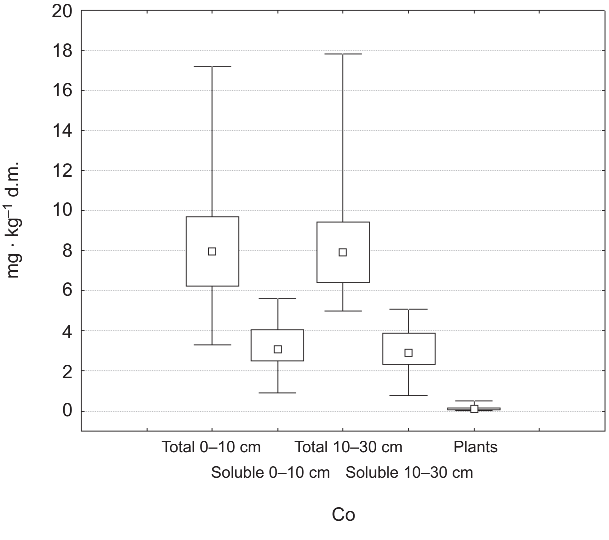

Fig. 3. Cobalt content in alluvial soils in 0–10 cm and 10–30 cm layer and in plants

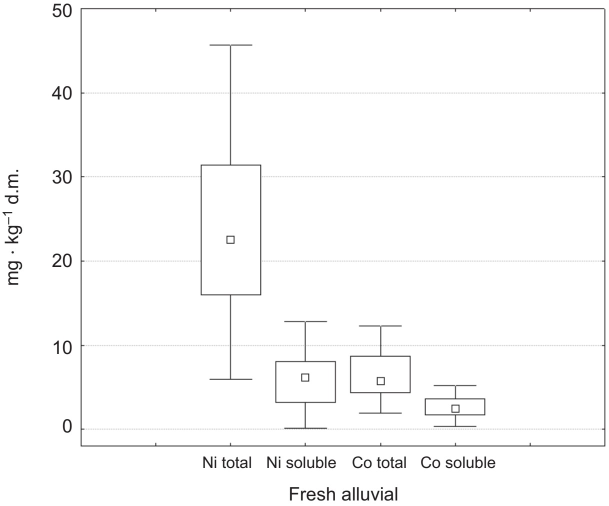

Fig. 4. Nickel and cobalt content in fresh alluvial

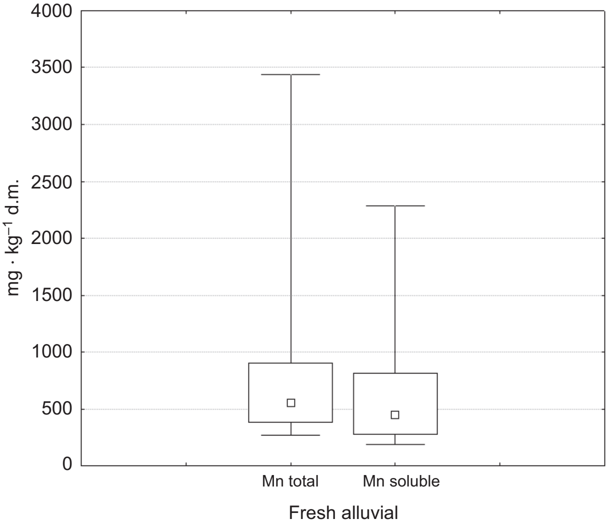

Fig. 5. Manganese content in fresh alluvial

Differences in content of total cobalt within single layers were meager. Geometric mean for turf layer was 7.84 mg · kg^{-1} d.m. and for under-turf equaled 8.1 mg · kg^{-1} d.m. (Table 2). Despite that the maximal values were about 18 mg · kg^{-1} d.m., so however upper quartiles in both layers laid under 10 mg · kg^{-1} d.m. (Fig. 3).

Geometric mean content of cobalt in grassland vegetation was 0.09 mg · kg^{-1} d.m. while upper quartile equaled 0.16 mg · kg^{-1} d.m. and was significantly lower than other maximal values (0.52 mg · kg^{-1} d.m.) (Fig. 3).

Geometric mean of total nickel content in fresh alluvial was 21.24 mg · kg^{-1} d.m. However, the content of soluble forms was significantly lower (Fig. 4). It can result from neutral reaction in studied soils.

Content of total cobalt in fresh alluvial was a little bit lower than in studied soils. Geometric mean equaled 6.04 mg · kg^{-1} d.m. of soil (Fig. 4).

Total Mn content in fresh alluvial ranged in broad scope of 270–3437 mg · kg^{-1} d.m. It should be underlined that upper quartile was 904 mg · kg^{-1} d.m. (Fig. 5). Because of very broad range within results there was calculated a quantile 97.5 which separated 2.5 % the upper values from 5 % which could lay outside a border of error. This value was 1818 mg · kg^{-1} d.m. The content which equaled three thousand was rare.

Discussion

Nickel is bound geochemically with iron and cobalt and its content in soils depends on loam minerals as well as organic matter content.

Nickel solubility increases along with acidification of soils. Mean content of this element in Polish soils is according to Kabata-Pendias and Pendias [2] 4–50 mg · kg^{-1} d.m., so the content of this element in studied soils ranged within the quoted scope.

Mean manganese content for different soils types in Poland are 100–1300 mg · kg^{-1} d.m. according to Kabata-Pendias and Pendias [2]. In conducted studies, the alluvial soils in the San River valley did not diverge from the mentioned scope.

Even determined maximum (1059 mg · kg^{-1} d.m.) was lower than upper mean values quoted by mentioned authors. Only the maximum values in fresh alluvial were higher.

As a minimal manganese content in grassland vegetation Falkowski et al [3] point out 10–20 mg · kg^{-1} d.m., while Borowiec and Urban [4] claim that optimal value is significantly higher ie 50–100 mg · kg^{-1} d.m. The variability of manganese content in studied grassland vegetation from the San River valley ranged from 16.8 to 228.8 mg · kg^{-1} d.m. and geometric mean equaled 46.82 mg · kg^{-1} d.m. The studied vegetation reached minimum values but quite often manganese content was in minus against optimal ones.

Kabata-Pendias and Pendias [2] say that in alluvial soils of Poland total cobalt content ranged from 5.5 to 19.0 mg · kg^{-1} d.m. Borowiec and Urban [4] in studied grassland soils from Lubelszczyzna, including alluvial soils, determined cobalt content in range from trace values to 3.3 mg · kg^{-1} d.m. In own research total cobalt amount was near to the values pointed out by the first authors. The scope of this content for both layers ranged from 3.3 to 17.81 mg · kg^{-1} d.m. Content of cobalt in its soluble fraction ranged from 0.8 to 5.6 mg · kg^{-1} d.m.

In good quality fodder according to Falkowski et al. [3] there should be minimum 0.08 mg Co · kg^{-1} d.m. whereas Borowiec and Urban [4] claim that the good content is when a value exceeds 0.1 mg Co · kg^{-1} d.m., and when the values reach less than 0.05 mg · kg^{-1} d.m. the content is too low. Grassland vegetation from the San River valley had usually a sufficient content of this element.

The content of the mentioned elements in fresh alluvial was similar to content in alluvial soils, so the fresh alluvial may be treated as a source of these elements however this enrichment is non-toxic.

The calcium carbonate is basic compound in carbonate buffer with especially big buffer capacity, so the mobility of some elements may be limited. The content of studied elements in plants was present in admissible amount if about animals feeding and sometimes diverged slightly in minus as in case of manganese.

Conclusions

1. Nickel, manganese and cobalt content in alluvial soils from the San River valley did not diverge from the background amount for soils in Poland.
2. Grassland vegetation from marshy meadows did not exceed admissible standards if about animals feeding and in some cases eg manganese there was possible to point out slight shortages.
3. Fresh alluvial were rich in studied elements and can be treated as a source of biogenic elements especially such as calcium.
4. The farming on terrains under floods must be fit to natural river functioning which features a seasonal floods resulting in creation on the surface a valuable fresh alluvial.

References

[1] Ostrowska A, Gawliński S, Szczubiałka Z. Metody analizy oceny właściwości gleb i roślin – Katalog. Warszawa: Wyd Inst Ochr Środ; 1991.
[2] Kabata-Pendias A, Pendias H. Biogeochemia pierwiastków śladowych. Warszawa: Wyd Nauk PWN; 1999.
[3] Falkowski M, Kukułka I, Kozłowski S. Właściwości chemiczne roślin łąkowych. Poznań: Wyd AR w Poznaniu; 1990.
[4] Borowiec J, Urban D. Środowisko przyrodnicze Lubelszczyzny. Łąki cz. II. Kondycja geochemiczna siedlisk łąkowych Lubelszczyzny. Lublin: LTN; 1997.

WYBRANE MIKROELEMENTY W GLEBACH I ROŚLINACH ŁĄK ŁĘGOWYCH DOLINY SANU

Katedra Przedsiębiorczości, Zarządzania i Ekoinnowacyjności, Wydział Zarządzania
Politechnika Rzeszowska

Abstrakt: Badania prowadzono na terenie użytków zielonych zlokalizowanych na obszarach zalewowych doliny Sanu. Badano zawartość Ni, Mn i Co w glebach oraz roślinności ekosystemów łęgowych. W badanych glebach oznaczono całkowitą zawartość badanych pierwiastków oraz zawartość ich form rozpuszczalnych w 1 mol HCl $\cdot$ dm^{-3}.

Gleby aluwialne i ruń łąkowa charakteryzowały się naturalną zawartością badanych pierwiastków. Świeże namuły były zasobne w badane pierwiastki oraz węglan wapnia.

Słowa kluczowe: gleby aluwialne, nikiel, mangan, kobalt, dolina Sanu

DOI: 10.2428/ecea.2012.19(01)0011 ECOL CHEM ENG A. 2012;19(1-2):105-111

Stanisław MERCIK[1] and Wojciech STĘPIEŃ[2]

EFFECT OF NITROGEN ON CROP YIELD AS INFLUENCED BY SOIL pH AND FERTILIZATION WITH FARMYARD MANURE

DZIAŁANIE AZOTU NA PLONOWANIE ROŚLIN W ZALEŻNOŚCI OD ODCZYNU GLEBY ORAZ NAWOŻENIA OBORNIKIEM

Abstract: At the Experimental Station of the Agriculture and Biology Department of Warsaw University of Life Sciences in Skierniewice fertilization experiments have been carried out continuously since 1923, in which the effects of lime, nitrogen, phosphorus, potassium and farmyard manure are studied in a static system with rotation of a few crops. Farmyard manure has been applied on a very acidic soil with a pH of about 4, and on a slightly acidic soil with a pH of 6.0–6.5. This paper describes only the results from combinations with and without nitrogen fertilization in the fields without FYM (since 1923) and with FYM (since 1992). The results presented here include the mean for 4 years yields of potatoes (fertilized with FYM) and grain crops grown in successive years following farmyard manure applications. Included are also the most important properties of the soils sampled in the last year after treatments with farmyard manure.

Yield increases resulting from nitrogen fertilization were very high and generally higher in the fields without manure than those with manure. The presence of farmyard manure was found to increase the organic carbon content and total nitrogen content in the soil by about 10 %. This type of fertilizer caused higher increases in yield in the combinations without nitrogen fertilization than in those involving applications of nitrogen.

Keywords: yield, long-term fertilizer experiment, soil organic carbon, forms of soil nitrogen

The utilization of nitrogen from nitrogen fertilizers generally fluctuates in the range of 55–65 %, but often the effect of that component is worse, which due to the high prices of such fertilizers makes their use less cost-effective. Good results with nitrogen are mainly achieved not only in favourable climatic conditions, but also in

---

[1] University Mazuriensis in Olecko, pl. Zamkowy 5, 19–400 Olecko, Poland, phone: +48 87 520 36 44, email: uczelniaKariera@gmail.com, www.wm.olecko.pl

[2] Department of Soil Environment Sciences, Division of Agricultural Chemistry, Warsaw University of Life Sciences, ul. Nowoursynowska 159, 02–686 Warszawa, Poland, phone: +48 22 593 26 30, email: wojciech_stepien@sggw.pl

soil conditions that are best-suited to the requirements of a given plant species. For that reason, nitrogen can be expected to produce good results if the soil has not been excessively depleted of humus and is not strongly acidified. The influence of these factors on the effectiveness of nitrogen can best be seen in long-term experiments [1–5].

The authors of this paper have at their disposal the results of long-term fertilization experiments, in which the effect of nitrogen on various crop plants has been studied over many years. The studies have been carried out on both strongly and weakly acidic soils, on which there have been no applications of farmyard manure since 1923, or in the fields where fertilization with FYM began in 1992. An assessment of the effects of these factors on the yields of a few species of crop plants and on the most important soil properties from theoretical and practical points of view seemed to be very interesting.

Materials and methods

At the Experimental Station of the Agricultural and Biology Department of Warsaw University of Life Science in Skierniewice, fertilization experiments have been carried out continuously since 1923, in which the effects of lime, nitrogen, phosphorus, potassium and farmyard manure are studied in a static system with rotation of a few crops. The experiments are conducted in 21 fields, where the total number of experimental plots (~50 m^2 each) is 650. This paper describes only the results from the combinations with and without nitrogen fertilization in those fields where crops are grown, without papilionaceous plants and without manure. The experiments are carried out on a podsolic soil containing 15–17 % of leachable components in the Ap horizon (0–25 cm) and 25 % in the B and C horizons. For the purpose of this study, 4 fields were chosen, including 2 fields with a very acidic soil (pH about 4), and 2 fields with a weakly acidic soil (pH 6.0–6.5). In one field with the very acidic soil, and in one field with the weakly acidic soil, fertilization with farmyard manure began in 1992 and continued every 4 years at a rate of 30 $Mg \cdot ha^{-1}$. By 2008 there had been four applications of manure for growing potato, and the next year, after the potato crop, cultivation included spring triticale, oat and rye on the very acidic soil, and spring barley, mustard and triticale on the weakly acidic soil. The results presented here are 2-year average yields. Over the period of 85 years, the application rates of mineral fertilizers increased from N-30, P-13, K-25 $kg \cdot ha^{-1}$ to N-90, P-26, K-91 $kg \cdot ha^{-1}$ from 1976. The fields with the weakly acidic soil are limed every 4 years at a rate of 1.6 Mg CaO per ha. In the fields with the very acidic soil, lime had been applied only five times over the 85-year-long period at a rate of 0.8 Mg CaO per ha. From the experimental plots described above soil samples were taken in the last year after farmyard manure application to determine: pH_{KCl}, hydrolytic acidity (Kappen's method), organic carbon (dry distillation), total nitrogen (Kjeldahl's method), and mineral nitrogen ($N\text{-}NH_4$ + + $N\text{-}NO_3$) in 0.1 mol $CaCl_2$.

Results and discussion

As had been expected, the extent of soil acidification depended mainly on lime application, and to a lesser degree also on nitrogen fertilization (Table 1). The soil of the plots limed only occasionally with small doses during 85 years is very acidic with a very high hydrolytic acidity (37 mmol $H^+ \cdot kg^{-1}$). With regular application of lime every 4 years, the value of soil pH fluctuated in the range of 5.5–6.5, depending on the year after liming, with hydrolytic acidity of 10–15 mmol $H^+ \cdot kg^{-1}$. Regular applications of ammonium nitrate also resulted in soil acidification. For example, on the plots without liming and without nitrogen fertilization, soil pH is higher by about 0.6, and hydrolytic acidity lower by about 12 mmol $H^+ \cdot kg^{-1}$ than on the plots fertilized with nitrogen. A somewhat smaller effect of nitrogen fertilization on soil acidification was obtained on limed plots. A small reduction in soil acidification was also obtained on farmyard manure plots. The acidifying effect of nitrogenous fertilizers and the mitigating effect of farmyard manure on soil acidification were also reported by other authors [2, 6–9].

Humus content in the soil depended mainly on the fertilization with farmyard manure, and also on nitrogen fertilization and liming. The highest increase in the organic C content in the soil resulting from four applications of manure since 1992 was obtained on the very acidic soil fertilized with nitrogen (Table 1). By taking into account an average increase in $C_{org.}$ due to FYM (0.41 $g \cdot kg^{-1}$) and the carbon dose in the manure (~16 $Mg \cdot ha^{-1}$), it was possible to calculate that about 10 % of the carbon from the manure was found in the soil. In other experiments on the same soil, but lasting much longer, the humification coefficient was within the 6–8 % range [3, 10, 11]. Only in short-term experiments, much more C_{org} from manure could be found in the soil [6, 7].

Table 1

Soil properties at the last year after FYM application depending on long-term fertilization

Soil properties	FYM since 1992	Fertilization since 1923			
		PK	NPK	CaPK	CaNPK
pH	O	4.5	3.9	6.5	6.1
	FYM	4.8	4.1	6.6	6.3
Hh [$mmol \cdot kg^{-1}$]	O	25.8	37.5	10.8	11.6
	FYM	24.5	37.7	12.2	14.5
C organic [$g \cdot kg^{-1}$]	O	3.91	4.51	4.22	4.62
	FYM	4.19	5.04	4.60	5.08
N total [$g \cdot kg^{-1}$]	O	0.35	0.43	0.38	0.45
	FYM	0.40	0.49	0.41	0.48
N mineral [$mg \cdot kg^{-1}$]	O	41.5	40.2	42.3	52.1
	FYM	48.6	51.6	48.5	63.5
C:N	O	11.2	10.5	11.1	10.3
	FYM	10.5	10.3	11.2	10.6

Hh – hydrolytic acidity.

With the passing of time from the last manure application, less and less $C_{org.}$ from that FYM, fertilizer remains in the soil. What needs to be emphasized, however, is the fact that nitrogen fertilization had an even greater effect on $C_{org.}$ content in the soil than farmyard manure. The plots fertilized with ammonium nitrate had higher levels of C_{org} in the soil by on average of $0.57\ g \cdot kg^{-1}$, with the increase being as much as $0.67\ g \cdot kg^{-1}$ in the very acidic soil. This means that fertilization with nitrogen considerably increased the yields of crop biomass, including the yields of post-harvest crop residue. The smallest effect on C_{org} increase in the soil was that of liming, on average by only $0.22\ g \cdot kg^{-1}$. This may have been due to the fact that, as the available literature indicates, liming contributes to the mineralization of humus.

The ratio of carbon to nitrogen in the soil was similar for all the experimental combinations. This indicates that the direction of the changes in total N in the soil, as affected by the factors studied, was very much like that of the $C_{org.}$ changes.

The differences in mineral nitrogen content ($N\text{-}NH_4$ + $N\text{-}NO_3$) in the soil were greater than those in total nitrogen. In all the combinations with FYM, the levels of mineral nitrogen were higher (Table 1). Lime applications also increased mineral N content in the soil, but only on the plots fertilized with nitrogen. Nitrogen fertilization also increased mineral N content in the soil, but only in the limed field. As is evident from the available literature, the mineral nitrogen content in the soil depends not only on the factors listed above [12–17], but also, and perhaps above all, on the time during the growing season when the soil samples are taken for analysis [13, 18].

The yields of plants grown on the soil fertilized with neither nitrogenous fertilizers nor manure for dozens of years were very low – about $9\ Mg \cdot ha^{-1}$ of potato tubers and $1.0–1.5\ Mg \cdot ha^{-1}$ of grain from cereals (Table 2). At such yields, the uptake of nitrogen from the soil did not exceed $30\ kg\ N \cdot ha^{-1}$, and these amounts of nitrogen could have come from atmospheric precipitation and the activity of free-living bacteria. Similar rates of nitrogen uptake from the soil in combinations which had not been fertilized with nitrogen were obtained in other experiments [11, 16, 19]. Farmyard manure used in amounts similar to the national average rate ($7.5\ Mg \cdot ha^{-1}$ annually) increased the yields of potato tubers to $15\ Mg \cdot ha^{-1}$ and the yields of cereal grains to $1.2–2.0\ Mg \cdot ha^{-1}$. These results indicate the levels of yielding that we should expect if we continue to cultivate crops for a long period of time without mineral fertilizers. To obtain higher yields on such farms, papilionaceous plants would have to be included in crop rotation.

Very low yields of spring triticale were obtained on the plots without nitrogen fertilization and that is why the increases in yield influenced by this component, in the limed field, were the highest. In the other grain crops, the effect of nitrogen was also large. The yields from the plots fertilized with nitrogen were more than twice as high as those from the plots without nitrogen fertilization. What can also be noted is that the effect of nitrogen was in most cases higher in the field without FYM than in the manured field. The yield-enhancing effect of manure was dependent not only on nitrogen fertilization but also on soil acidity and the species of the cultivated plant. The increases in the yields of almost all the crop plants (except potatoes and spring triticale on the acidic soil) influenced by manure on the plots without nitrogen were higher than on the plots fertilized with nitrogen. The relationship for potatoes and spring triticale is greater in limed fields than on a very acidic soil. The literature [8, 9, 20] says that the yield-enhancing effect of nitrogen will be significant only if the growth of plants is not inhibited by strong acidification of the soil.

Table 2

Yield of plants depending on long-term fertilization and manuring (FYM) on the limed and unlimed soils (mean of 4 years)

Plants	Fertilization since 1923	$Mg \cdot ha^{-1}$		%, CaPK, PK =100		FYM increased %
		–FYM	+FYM	–FYM	+FYM	
Potato	PK	5.51	9.29	100	100	68.6
	NPK	7.12	12.54	129.2	135.0	76.1
	CaPK	8.7	16.5	100	100	89.7
	CaNPK	19.1	23.6	219.5	143.0	23.6
	LSD	0.49	0.52			
Spring triticale	PK	0.93	1.16	100	100	24.7
	NPK	1.22	1.69	131.2	145.7	38.5
	CaPK	0.96	1.34	100	100	39.6
	CaNPK	3.12	3.14	325.0	324.3	0.6
	LSD	0.21	0.23			
Oat	PK	1.21	1.85	100	100	52.9
	NPK	3.34	3.70	279.0	200	10.8
	LSD	0.19	0.24			
Rye	PK	1.52	2.02	100	100	32.9
	NPK	3.89	4.26	255.9	210.9	9.5
	LSD	0.25	0.27			
Spring barley	CaPK	1.35	2.03	100	100	50.4
	CaNPK	2.91	3.56	215.6	175.4	22.3
	LSD	0.24	0.27			
Mustard	CaPK	0.57	0.85	100	100	49.1
	CaNPK	1.58	2.00	277.2	235.3	26.7
	LSD	0.17	0.21			

$LSD_{(0.05)}$ – only for N fertilization.

The soil of the plots without nitrogen fertilization (PK and CaPK) is sufficiently rich in available forms of phosphorus and potassium, and thus it can be inferred that the effect of farmyard manure may be dependent mainly on a good supply of nitrogen to plants. In comparison with the effect of nitrogen from mineral fertilizers, the after-effect of the nitrogen from manure is also greater, especially of that applied for many years. This is demonstrated by the fact that in the last year after the application of manure there is more total and mineral nitrogen in the manured than non-manured field (Table 1).

Conclusions

1. Applications, of farmyard manure, every four years, increased organic carbon and total nitrogen content by about 10 %.
2. Ammonium nitrate used over many years reduced soil pH and increased hydrolytic acidity of the soil.
3. Yield increases influenced by nitrogen fertilization were very high and in most cases higher on the non-manured than manured plots.
4. The effect of farmyard manure on crop yield was in most cases greater on the plots without rather than with nitrogen fertilization.

References

[1] Ciećko Z, Wyszkowski M, Szagała I. Zesz Probl Post Nauk Rol. 1996;440:27-33.
[2] Fotyma E. Nawozy i Nawożenie. 2000;3a:17-35.
[3] Janowiak J, Spychaj-Fabisiak E, Murawska B. Fragm Agron. 2004;1:78-87.
[4] Jenkinson DS, Bandbury N J, Koleman K. How the Rothamsted classical experiments have been used to develop and test models for the turnover of carbon and nitrogen in soil. Long-term Experiments. In: Agricultural and Ecological Sciencies, Cab International. 1994;7:117-138.
[5] Johnston A. The Rothamsted Classical Experiments. Long-term Experiments in Agricultural and Ecological Sciencies, Cab International. 1994;2:9-37.
[6] Łabętowicz J, Kuszelewski L, Korc M, Szulc W. Zesz Probl Post Nauk Rol. 1999;465:123-134.
[7] Mercik S, Stępień W, Sosulski T. Zesz Probl Post Nauk Rol. 1999;465:71-80.
[8] Mercik S, Łabętowicz J, Sosulski T, Stępień W. Nitrogen Workshop, Reims, France: 2001;303-304.
[9] Mercik S, Łabętowicz J, Sosulski T. Nawozy i Nawożenie. 2002;IV:228-237.
[10] Mercik S, Mazur T, Łabętowicz J, Urbanowski S, Lenart S, Stępień W, Sądej W. Zesz Probl Post Nauk Rol. 2003;494:295-303.
[11] Mercik S, Stępień M, Pietrzak S. Zesz Probl Post Nauk Rol. 2004;499:253-261.
[12] Mercik S, Stępień W. Fragm Agron. 2005;1(85):189-201.
[13] Mercik S, Stępień W, Sosulski T. Rocz Gleb. 2005;LVI:53-59.
[14] Mercik S, Stępień W. Zesz Probl Post Nauk Rol, 2007;520:151-158.
[15] Schmidt L, Warnstoff K, Dorfel H, Leinweber P, Lang H, Merbach W. J. Plant Nutr Soil Sci. 2000;136:639-648.
[16] Sosulski T, Stępień W, Szara E, Mercik S. Fragm Agron. 2005;1(85):264-273.
[17] Stępień W, Mercik S, Sosulski T. Zesz Probl Post Nauk Rol. 2002;484:223-230.
[18] Stępień M, Mercik S, Stępień W. Nawozy i Nawożenie. 2002;4:211-219.
[19] Weigel A, Kubat J, Korschens M, Powlson D, Mercik S. Arch Acker PFl. Boden. 1998;43:123-143.
[20] Wiater J, Chwil S. Fragm Agron, 2005;1:613-623.

DZIAŁANIE AZOTU NA PLONOWANIE ROŚLIN W ZALEŻNOŚCI OD ODCZYNU GLEBY ORAZ NAWOŻENIA OBORNIKIEM

Katedra Nauk o Środowisku Glebowym
Szkoła Główna Gospodarstwa Wiejskiego w Warszawie

Abstrakt: W Stacji Doświadczalnej Wydziału Rolnictwa i Biologii SGGW w Skierniewicach nieprzerwanie od 1923 r. prowadzone są doświadczenia nawozowe, gdzie bada się działanie wapna, azotu, fosforu, potasu i obornika w układzie statycznym w kilku zmianowaniach roślin. Obornik stosuje się na glebie bardzo kwaśnej o pH około 4 oraz słabo kwaśnej o pH 6,0–6,5. W niniejszej pracy zamieszczono wyniki badań uzyskane tylko z obiektów nawożonych i nienawożonych azotem, na polach bez obornika (od 1923 r.) i z obornikiem (od 1992 r.). Uzyskane dane obejmują średnie z 4 lat plony ziemniaków (nawożonych obornikiem) oraz plony roślin zbożowych uprawianych w kolejnych latach po oborniku. Zamieszczono również najważniejsze właściwości gleb pobranych w ostatnim roku po oborniku.

Zwyżki plonów pod wpływem nawożenia azotem były bardzo duże i przeważnie większe na polach bez obornika niż z obornikiem. Obornik zwiększał zawartość węgla organicznego i azotu ogólnego w glebie o około 10 %. Nawóz ten bardziej zwiększał plony na obiektach nienawożonych azotem niż na kombinacjach, gdzie stosowano ten składnik.

Słowa kluczowe: wieloletnie doświadczenia nawozowe, plony roślin, węgiel organiczny, formy azotu w glebie

DOI: 10.2428/ecea.2012.19(01)012 ECOL CHEM ENG A. 2012;19(1-2):113-121

Marcin NIEMIEC[1], Barbara WIŚNIOWSKA-KIELIAN[1]
and Monika ARASIMOWICZ[1]

CONTENTS OF COPPER, NICKEL AND CHROMIUM IN THE SEDIMENTS OF RAINWATER RESERVOIRS SITUATED ALONG THE NATIONAL ROAD No. 4

ZAWARTOŚĆ MIEDZI, NIKLU I CHROMU W OSADACH ZBIORNIKÓW WÓD DESZCZOWYCH USYTUOWANYCH WZDŁUŻ DROGI KRAJOWEJ Nr 4

Abstract: The paper aimed at determining heavy metal pollution level of the sediments collected from reservoirs that retain rainwater, localized along the national road No. 4. The sediments were sampled from 11 reservoirs on three dates: in May 2007, in April 2008 and in June 2008 in the Sulkow, Biskupice, Bodzanow and Suchoraba villages, along the *ca* 10 km section of this road. The sediments were dried in the open air, dry-mineralized and dissolved in a mixture of nitric and chloric acids (3:2, v/v). The contents of copper, chromium and nickel were assessed in the obtained solutions by means of ICP-AES method.

Copper contents in the analyzed sediments ranged from 9.29 to 102 mg $\cdot$ kg^{-1}, with an average for all samples 34.94 mg Cu $\cdot$ kg^{-1}. Chromium contents in the studied sediments comprised in limits 12.6–58.1 mg Cr $\cdot$ kg^{-1}, with an average value of 27.7 mg Cr $\cdot$ kg^{-1}. Nickel quantities assessed in sediments from rainwater reservoirs were within the range of 7.57–25.62 mg Ni $\cdot$ kg^{-1}, with an average value of 13.71 mg $\cdot$ kg^{-1}. Changeability (RSD) of the studied metal contents between individual reservoirs fluctuated from 18 to 58 %. The amounts of analyzed elements in the sediments from reservoirs receiving runoffs from the road were much smaller than assessed in similar sediments from various cities worldwide. The investigated sediments do not pose any hazard in view of pollution with copper, chromium or zinc. A regular diminishing of copper content in the sediments was observed with increasing distance from Krakow agglomeration. The closest reservoir is situated in Sulkow, 7 km from the Krakow boundaries, near the boundaries of the Wieliczka town. On the other hand, the reservoir in Suchoraba village is about 17 km far from Krakow. Along this stretch copper content in sediment taken from reservoirs that retain rain water diminished several times, what points at a considerable effect of pollution coming from urban centre on this metal level in the sediments. No such dependence was observed for nickel or chromium.

Keywords: rainwater reservoirs, sediments, metals content, Cu, Ni, Cr

---

[1] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone: +48 12 662 43 47, fax +48 12 662 4341, email: niemiecm@tlen.pl, rrkielia@cyf-kr.edu.pl

Advanced level of urbanization increases the number of hard surfaced areas. With growing area of anthropogenically transformed terrains the hazard of area pollution source is more serious. *Environmental Protection Agency* (EPA) attaches more attention to this type of pollution which may locally lead to environment degradation. Many researchers of this problem state that in the areas with high coefficient of urbanization rainwater is currently the gravest threat to both surface and underground water quality [1–3]. Rainwater running off from hard surfaced areas may contain considerable amounts of pollutants posing a hazard to natural ecosystems [4]. The most important impurities polluting the runoffs are organic matter, heavy metals, oil derivatives, chlorides which can be extracted with petroleum spirit [5]. The Directive of the Minister of Environment of 29 November 2002 [6] determines the necessity to clean rainwater from the road drainage to make it parameters would meet the standards formulated in the Directive of the Minister of Environment of 24 July 2006 [7]. One of the ways of pretreatment is the use of sedimentation pools and infiltration and evaporation tanks. Various physical and physicochemical phenomena are used in these devices to remove the pollutants from rainfall wastewater and transform them to sediments [8]. It is thought that bioretention reservoirs are the most efficient method of cleaning rainwater runoffs of heavy metals, because the physical and chemical processes are supplemented with biological sorption of pollutants. Another problem is treatment and disposal of water from the pretreatment reservoirs. Inappropriate exploitation and utilization of the reservoirs may after some years cause mobilization of toxicants bound in the sediments posing a hazard to the natural environment. With increasing number of facilities pretreating stormwater sewage the pressure of roads and other urbanized areas on the environment will be diminishing, but also considerable amount of sediments will be generated and their management may prove problematic. The annual deposition of sediments from surface runoffs in France is estimated for 5 million Mg (tons) and potentially increasing in future [3].

Heavy metals are constant component of rainfall water. Emission of these elements to the environment is connected with all kinds of human activity. Metals are emitted to the atmosphere, absorbed on dust particles fall to the ground from where are washed away by rainwater. Considerable amounts of nickel find their way to the environment with burning fuels and this element leaching from the road surface, but also due to corrosion of vehicle parts coated with this element. Chromium in rainfall sewage also comes from fuel burning and in result of leaching from chromium plated vehicle surfaces.

The investigations aimed at determining the extent of copper, chromium and nickel pollution of sediments from the reservoirs of rainwater running from the surface of national road No. 4.

Material and methods

In 2007 and 2008 sediments were sampled from evaporation reservoirs which receive rainwater runoffs from the national road No. 4 along *ca* 10 km section of this road between Sulkow and Suchoraba villages. The parameters of the reservoirs and the catchment were given in Table 1.

Table 1

Characteristic of stormwater ponds

No.	No. of object	Localization	Capacity of reservoir [V]	Retention time of water in pond [t]	Total catchment area		Flow [Q]
					sealed [F_1]	green areas [F_2]	
			[m^3]	[min]	[ha]	[ha]	[$dm^3 \cdot s^{-1}$]
1	20	Sulkow	118.4	31.1	0.29	1.85	71
2	21	Sulkow	176.9	29.4	0.29	5.97	119
3	22	Sulkow	86.2	29.7	0.18	2.67	58
4	33	Biskupice	93.0	24.2	0.39	2.58	77
5	32	Przebieczany	81.5	37.8	0.17	1.29	45
6	36	Bodzanow	98.0	25.8	0.62	0.69	87
7	37	Bodzanow	127.0	30.4	0.39	4.08	127
8	41	Suchoraba	101.6	27.2	0.36	2.64	95
9	43	Suchoraba	—	—	0.37	3.88	94
10	45	Suchoraba	194.8	32	0.36	5.17	119
11	55	Suchoraba	218.0	27.7	0.53	9.91	156

The samples were collected on three dates: in May 2007, in April 2008 and in June 2008 in the Sulkow, Biskupice, Bodzanow and Suchoraba villages. Sediments for analyses were sampled from 11 reservoirs situated in: Sulkowice – 3 reservoirs, Biskupice – 1 reservoir, Przebieczany – 1 reservoir, Bodzanow – 2 reservoirs and Suchoraba – 4 reservoirs. Average sample was composed of primary samples collected from the whole area of the reservoirs. A laboratory sample was representative for the whole reservoir. The sediments were gathered from the top layer to the depth of 10 cm. Collected sediments were dried in the open air, dry mineralized in a muffle furnace at 450 ^{o}C and digested in a mixture of $HClO_4$ and HNO_3 acids (2:3, v/v). Material prepared in this way was dissolved in HCl and the contents of copper, chromium and nickel were assessed in obtained solution using ICP-AES method on JY 238 ULTRACE apparatus (Jobin Yvon Emission). Organic matter content was determined on the basis of weight loss during calcinations at 550 ^{o}C. The methods were validated on the basis on internal reference materials.

Rainwater sewage pollution with copper is mainly connected with fuel burning in engines. It has been estimated that cars emit about $4.5 \cdot 10^{-5}$ g per 1 kilometre of the way they pass [8]. Considerable amounts of this element are frequently noted in runoffs from roads and highways. Nordeidet et al [9] emphasize great importance of copper as a factor polluting runoffs from roads and highways.

Average copper content in the sediments from rainwater reservoirs was 34.94 $mg \cdot kg^{-1}$, fluctuating from 9.29 to 102 $mg\ Cu \cdot kg^{-1}$ (Table 2). The greatest quantities were registered in the sediments from the third sampling, where the amount was almost

Table 2

Parameters of heavy metals quantity in sediments from stormwater ponds

Element	Following sampling	Minimum	Maximum	Mean	Median	RSD* [%]
		[mg · kg^{-1} d.m.]				
Cu	I	9.29	60.64	30.34	30.96	59
	II	12.18	57.30	29.43	26.94	57
	III	11.82	102.0	45.06	46.56	55
Cr	I	16.38	58.08	34.20	29.60	37
	II	12.62	26.31	20.89	18.06	35
	III	17.19	38.94	28.52	27.31	26
Ni	I	7.57	15.52	11.65	11.63	18
	II	11.31	25.62	16.88	14.56	30
	III	8.37	18.19	12.77	12.03	22

* RSD – *Relative standard deviation.*

twice greater than in the 1st or 2nd sampling. The highest concentrations of copper were determined in the reservoirs situated closest to Krakow (Fig. 1). The average for 1–6 objects for all three samplings was 42.26 mg · kg^{-1}, whereas for reservoirs 7–11 it reached 26.62 mg · kg^{-1}. With growing distance from the city agglomeration copper level in the sediments was decreasing regularly. Standard deviation for sediments from all reservoirs fluctuated from 50 to 60 % between the successive samplings.

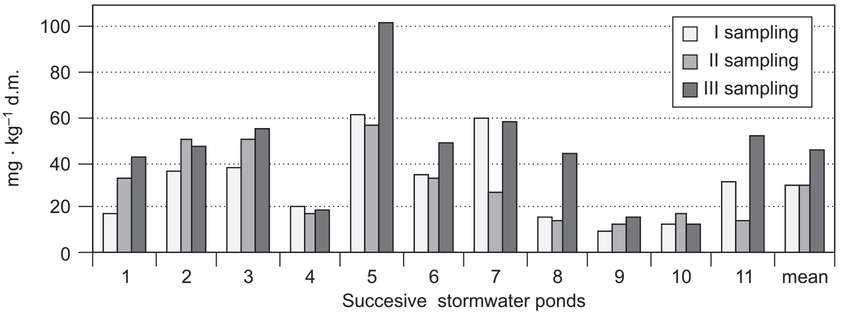

Fig. 1. Copper content in sediment from successive stormwater ponds

Copper contents in the analyzed sediments indicate their anthropogenic enrichment. This metal quantities registered by Neal et al [10] in the Thame River water (the Thames tributary) reached several mg · dm^{-3}. Wisniowska-Kielian and Niemiec [11] reported diversified copper contents in the sediments from the Dunajec River bottom and retention reservoirs: from 3.5 mg · kg^{-1} in the unpolluted areas to 28 mg · kg^{-1} in the regions under strong anthropopressure. However, copper concentrations assessed in the investigated sediments do not pose a hazard to the environment because they do not exceed the permissible contents of this element in soil or protected ground [6]. Nogaro et al [12] found that copper concentrations in reservoirs accumulating rainwater in the Lyon area reached the level of 113 mg · kg^{-1}. On the other hand, Rozenkrantz et al [13] assessed the copper contents in the sediments from rainwater infiltration pools in the vicinity of Melbourne similar to obtained in the presented research, amounting from 9.6 to 124 mg Cu · kg^{-1}, whereas Datry et al [14] observed a much higher concentration of this metal, between 241–503 mg · kg^{-1}, in the infiltration pools of rainwater runoffs in Lyon neighbourhood. Petavy et al [3] also registered high contents of copper in the sediments from infiltration pools in western France reaching from 122 to 334 mg · kg^{-1}, depending on the fraction. These authors pay attention to a considerable copper affinity to organic matter and the finest sediment fractions. These properties of copper cause that its removal from sediments depends the sedimentation conditions in reservoirs. Ikenaka et al [15] stated much higher quantities of copper in sediment of Kafue River, which ranged from 23 to 12906 mg · kg^{-1}, 4745 mg · kg^{-1} on average, whereas recommended value amounts 50 mg Cu · kg^{-1}. This phenomenon is a result of heavy metals transportation from the Copper Belt area to downstream areas. Krolikowski et al [16] noted copper concentrations amounting 6.8–60 mg · kg^{-1} in storm inlets in Bialystok, approximate to presented in this paper. Murakami et al [17] point to possible copper contamination of underground runoffs. These authors state that copper concentrations in the dust from the heavily loaded highways may reach even 990 mg · kg^{-1}. Mayer et al [18] report that this element concentrations in the sediments from reservoir receiving stormwater in Toronto range from 56 to 114 mg · kg^{-1}, *ie* are a bit higher than presented in the paper. Birch and McCready [19] investigated copper content in street dust and in the sediments from reservoirs accumulating rainwater in Sydney. Average copper content in street dust was 160 mg Cu, whereas in the sediments reached over 200 mg Cu · kg^{-1}. It evidences a considerable copper binding by organic matter and suspension particles. Obtained results of copper contents in sediments of the investigated reservoirs are much lower than presented by various authors.

Chromium content in sediments from the analyzed reservoirs ranged from 123.6 to 58.1 mg · kg^{-1} d.m. (Fig. 2) and was on average of 27.7 mg · kg^{-1}. The highest contents of this element were registered in the sediments collected in June 2008, whereas the lowest in sediments of the second sampling (April 2008).

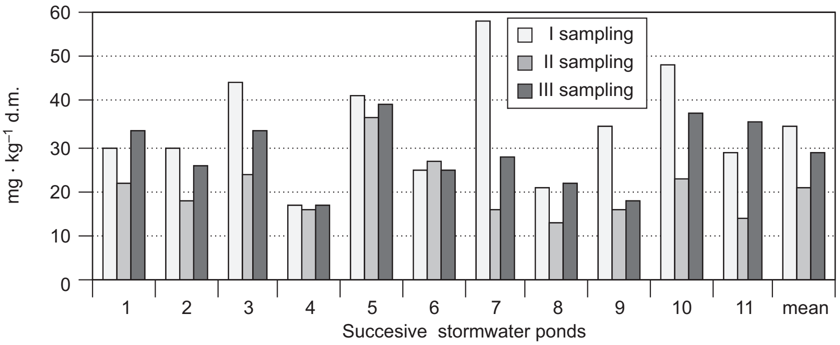

Fig. 2. Chromium content in sediment from successive stormwater ponds

No dependence of chromium concentration in sediments on the reservoir distance from Krakow was registered, as it had place in case of copper. Variability (RSD) of this element content in individual reservoirs was quite equal considering the sampling date and in all analyzed sediments fluctuated from 26 to 37 % (Table 2). Chromium contents in sediments of the studied reservoirs were not high and much lower than the literature data. No exceeded permissible content of this element was registered either in the soil or ground under protection [6]. Datry et al [14] determined chromium content in sediments from infiltration pools of rainwater runoffs in Lyon vicinity on the level of 68–129 mg · kg^{-1}, whereas Petavy et al [3] registered this metal contents in sediments from western France ranging from 33–113 mg · kg^{-1}. Birch and McCready [19] in their study determined chromium content in sediments originating from urbanized areas in Syndey amounting 31 mg · kg^{-1}. The same authors reported that this element content in street dust in Syndey equaled 34 mg · kg^{-1}. Jartun et al [20] assessed an average content of chromium in runoffs in Bergen, Norway as 30 mg · kg^{-1}, while McKenzie et al [21] report 122 mg · kg^{-1} as an average content of this metal in dust from highways in California. On the other hand, Krolikowski et al [16] registered average amounts of chromium in storm inlets in Bialystok ranging from 1.17 to 3.84 mg · kg^{-1}, whereas sediments from lamella separators from this city contained much larger amounts, 19.2–63.2 mg Cr · kg^{-1}. Chromium contents in the analyzed reservoirs sediments were small, much smaller than assessed in similar objects from the other parts of the world.

Nickel content in the researched sediments fluctuated from 7.57 to 25.62 mg · kg^{-1} and on average was 13.71 mg · kg^{-1} (Fig. 3). Average quantities of this element in sediments from all reservoirs differed slightly. The greatest amount of nickel was determined in the sediments collected in April 2008. No such relationship as in case of copper was noted between this element accumulation in the sediments and the reservoir distance from Krakow city agglomeration. Higher contents were registered only in sediments from the second sampling in the reservoirs numbered 1, 2 and 3. Variability of this element contents in individual reservoirs between sampling dates was slight and in all studied sediments fell within 18–31 % range (Table 2).

Nickel contents in the investigated sediments were low and did not exceed values permissible for soil or ground under protection [6].

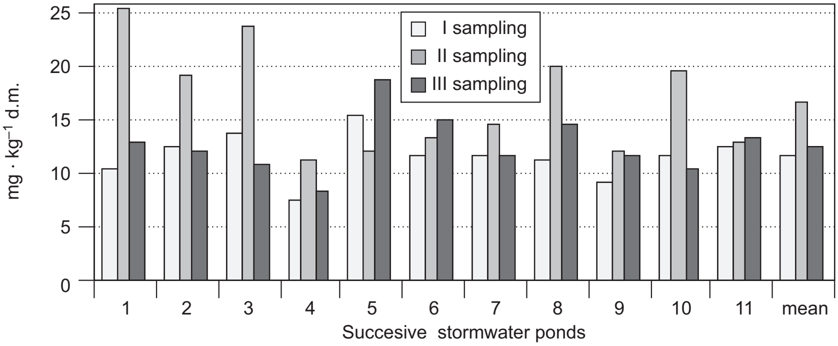

Fig. 3. Nickel content in sediment from successive stormwater ponds

Nickel is fairly common in the environment and is always a component of rainwater. This element contents in the analyzed sediments remained on a level formerly assessed by Wisniowska-Kielian and Niemiec [11] in bottom sediments of the Dunajec River and its tributaries. Nickel contents in sediments from the studied reservoirs were not high and much lower than presented in literature. Datry et al [14] stated this element content in sediments from infiltration pool of rainwater runoffs in the vicinity of Lyon ranging from 50 to 114 $mg \cdot kg^{-1}$, whereas Murakami et al [17] reported average concentrations of nickel of about 50 $mg \cdot kg^{-1}$ in street dust, which reached even 100 $mg \cdot kg^{-1}$ but only on highways with high traffic load. Birch and McCready [19] assessed 31 $mg\ Ni \cdot kg^{-1}$ in sediments originating in the urbanized areas in Sydney, whereas nickel content in street dust in this city was 34 $mg \cdot kg^{-1}$. Rozenkrantz et al [13] noted nickel contents of 5.7–21.5 $mg \cdot kg^{-1}$ in the sediments from rainwater infiltration pools in the vicinity of Melbourne, similar to obtained in the Authors' own research. Jartun et al [20] reported 24 $mg \cdot kg^{-1}$ as mean nickel content in the sediments from runoffs in Bergen, Norway. On the other hand, in research conducted by Krolikowski et al [16] average contents of this element in the sediments from storm inlets in Bialystok ranged from 0.98 to 12.8 $mg \cdot kg^{-1}$, but the amounts of this element assessed on lamella separators were 13–43 $mg \cdot kg^{-1}$.

The contents of the investigated metals in sediments from road runoffs were not high and it may be supposed that they do not pose any environmental hazard. The levels of copper, chromium and nickel in the sediments were much lower than observed by other authors in various cities in the world, however assessed ranges of these elements contents indicate anthropogenic enrichment of the sediments. The share of hard surfaced catchment in total area of the investigated reservoirs catchment is only from 5 to 10 %. The remaining part consists of green areas. Such considerable share of natural areas in total catchment area of the reservoirs leads to dilution of pollutants running off roads and their uptake by grass plants, which may explain lower contents of the studied impurities. Runoffs from city centres with considerable share of hard surfaced areas in catchment are always more burdened with pollutants. Barret et al [2] point to a considerable variability of the chemistry of runoffs from roads during rainfall. Sewage of the first phase of the runoff is the most concentrated. Its pollutant concentrations may be compared with those noted in industrial sewage, therefore retention reservoirs counteract the discharge of highly concentrated sewage to the natural, particularly water environment and their most important role is receiving the pollutants carried by the first phase of the runoff.

Conclusions

1. Sediments from the investigated rainwater reservoirs were characterized by a much lower content of copper, chromium and nickel than the sediments collected from rainwater reservoirs in various cities worldwide.

2. A high share of green areas in total catchment area of the studied reservoirs might favour lower accumulation of the studied metals in the sediments because waters filtering through green areas always contain lesser amounts of pollutants.

3. Copper contents in sediments of the analyzed reservoirs depended on the localization of the reservoir and were diminishing systematically with increasing distance from Krakow agglomeration boundaries. No such relationship was assessed for chromium and nickel.

References

[1] Lee PK, Touray J-C, Baillif P, Ildefonse J.P. Sci Total Environ. 1997;201:1-15.
[2] Barrett ME, Zuber RD, Collins ER, Malina JF, Charbeneau RJ, Ward GH. A Review and Evaluation of Literature Pertaining to the Quantity and Control of Pollution from Highway Runoff and Construction, 2nd edition. Center for Research in Water Resources, Bureau of Engineering Research, Austin, Texas: 1995.
[3] Pétavy F, Ruban V, Conil P. Chem Eng J. 2009;145(3):475-482.
[4] Vaze J, Chiew FH. Urban Water. 2002;4(4):379-389.
[5] Khan E, Khaodhir S, Ruangrote D. Bioresource Technol. 2009;100(19):4454-4461.
[6] Rozporządzenie Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi. Dz.U. 2002, Nr 165, poz. 1359.
[7] Rozporządzenie Ministra Środowiska z dnia 24 lipca 2006 r. w sprawie warunków, jakie należy spełniać przy wprowadzaniu ścieków do wód lub ziemi oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego. Dz.U. 2006, Nr 137, poz. 984.
[8] Ball DJ, Hamilton RS, Harrison RM. Highway Pollution, Hamilton RS, Harrison RM, editors. Studies Environ Sci. 1991;44:89.
[9] Nordeidet B, Nordeide T, Åstebøl SO, Hvitved-Jacobsen T. Sci Total Environ. 2004;334-335:231-238.
[10] Neal C, Neal M, Hill L, Wickham H. Sci Total Environ. 2006;360(1-3):254-271.
[11] Wiśniowska-Kielian B, Niemiec M. J Elementol. 2005;10(2):435-443.
[12] Nogaro G, Mermillod-Blondin F, Montuelle B, Boisson JC, Lafont M, Volat B, Gibert J. Chemosphere. 2007;70(2):315-328.
[13] Rosenkrantz RT, Pollino CA, Nugegod D, Baun A. Environ Pollut. 2008;156(3):922-927.
[14] Datry T, Malard F, Vitry L, Hervant F, Gibert J. J Hydrol. 2003;273(1-4):217-233.
[15] Ikenaka Y, Nakayama SMM, Muzandu K, Choongo K, Teraoka H, Mizuno N, Ishizuka ML. African J Environ Sci Technol. 2010;4(11):729-739.
[16] Królikowski A, Garbarczyk K, Gwoździej-Mazur J, Butarewicz A. Monografie Polskiej Akademii Nauk, Komitet Inżynierii Środowiska, Białystok: 2006.
[17] Murakami M, Fujita M, Furumai H, Kasuga I, Kurisu F. J Hazardous Mater. 2009;164(2-3):707-712.
[18] Mayer T, Rochfort Q, Borgmann U, Snodgrass W. Environ Pollut. 2008;156(1):143-151.
[19] Birch GF, McCready S. Sci Total Environ. 2009;407(1):2820-2835.
[20] Jartun M, Ottesen RT, Steinnes E, Volden T. Sci Total Environ. 2008;396(2-3):147-163.
[21] McKenzie ER, Wong CM, Green PG, Kayhanian M, Young T. Sci Total Environ. 2008;**398**(1-3): 145-153.

ZAWARTOŚĆ MIEDZI, NIKLU I CHROMU W OSADACH ZBIORNIKÓW WÓD DESZCZOWYCH USYTUOWANYCH WZDŁUŻ DROGI KRAJOWEJ Nr 4

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

Abstrakt: Celem pracy było określenie poziomu zanieczyszczenia metalami ciężkimi osadów pobranych ze zbiorników zlokalizowanych wzdłuż drogi krajowej nr 4 przyjmujących wody deszczowe. Osady pobrano z 11 zbiorników w trzech terminach: maj 2007 r., kwiecień 2008 r. i czerwiec 2008 r. z miejscowości: Sułków, Biskupice, Bodzanów i Suchoraba na odcinku ok. 10 km. Osady wysuszono na powietrzu i zmineralizowano na sucho i roztworzono w mieszaninie kwasów azotowego(V) i chlorowego(VII) w stosunku objętościowym 3:2. W uzyskanych roztworach oznaczono ogólną zawartość miedzi, chromu oraz niklu metodą ICP-AES.

Zawartość miedzi w badanych osadach mieściła się w granicach od 9,29 do 102 mg · kg^{-1}. Średnia dla wszystkich próbek wynosiła 34,94 mg · kg^{-1}. Stężenie chromu w badanych osadach wahało się w granicach 12,6–58,1 mg Cr · kg^{-1}, a średnio wynosiło 27,7 mg · kg^{-1}. Ilości niklu oznaczone w osadach ze zbiorników wód opadowych mieściły się w zakresie 7,57–25,62 mg Ni · kg^{-1}. Średnia zawartość tego pierwiastka wynosiła 13,71 mg · kg^{-1}. Zmienność (RSD) stężeń badanych metali pomiędzy poszczególnymi zbiornikami wahało się w granicach 18–58 %. Ilości badanych pierwiastków w osadach ze zbiorników przyjmujących spływy z drogi były znacznie mniejsze niż stwierdzane w podobnych osadach w innych miastach na świecie. Badane osady nie stanowią zagrożenia ze względu na zawartość miedzi, niklu i chromu. Zaobserwowano regularne zmniejszanie zawartości miedzi w miarę oddalania się od aglomeracji krakowskiej. Zbiornik usytuowany najbliżej Krakowa w Sułkowie oddalony jest o ok. 7 km od rogatek Krakowa i znajduje się przy granicy z miastem Wieliczka, natomiast zbiornik w Suchorabie jest oddalony o ok. 17 km od Krakowa. Na tym odcinku zawartość miedzi w osadach ze zbiorników wód deszczowych zmniejszyła się kilkakrotnie, co wskazuje na znaczny wpływ zanieczyszczeń napływających z ośrodka miejskiego na poziom tego metalu w osadach. W przypadku niklu i chromu nie zaobserwowano takiej zależności.

Słowa kluczowe: zbiorniki wód deszczowych, osady, zawartość metali, Cu, Ni, Cr

Magdalena SENZE[1] and Monika KOWALSKA-GÓRALSKA

PRESENCE OF METALS IN WATERS FROM SACRED SPRINGS IN EUROPE

OBECNOŚĆ METALI W WODACH ZE ŚWIĘTYCH ŹRÓDEŁ W EUROPIE

Abstract: Laboratory tests were carried out of water sampled from springs located at various towns throughout Europe: in Poland (Gierzwald and Ludzmierz), France (Lourdes, La Salette), Portugal (Fatima) and Greece (Ephesus). The following were determined for the samples: electrolytic conductivity, and copper, zinc, cadmium, lead and nickel concentrations. The waters in question had the reaction ranging from 7.64 pH to 8.15 pH. Electrolytic conductivity oscillated between 201.00 $\mu S \cdot cm^{-1}$ and 702.00 $\mu S \cdot cm^{-1}$. Metal contents were as follows: copper – 0.0001–0.0052 $mgCu \cdot dm^{-3}$, zinc – 0.0015–0.2153 $mgZn \cdot dm^{-3}$, cadmium – 0.0005–0.0012 $mgCd \cdot dm^{-3}$, lead – 0.0000–0.0101 $mgPb \cdot dm^{-3}$ and nickel – 0.0000–0.0017 $mgNi \cdot dm^{-3}$. The tests showed that the waters in question, which are believed by pilgrims to possess medicinal and healing properties, met the criteria established for water intended for human consumption.

Keywords: water, metals, sacred springs

Waters from sacred springs around the world are regarded as special, due to their reputed medicinal, healing and converting properties. Usually they are sampled by pilgrims to be drunk as potable water. They are also used by the sick to wash ailing parts of the body. Frequently the sick can also have a bath in sacred waters.

Europe has numerous places which, due to religious worship (the presence of relics, miraculous healing), are regarded by pilgrims as particularly important and worth visiting. Such sanctuaries are often located at small towns or villages, on slopes of hills, far from big cities. Apart from their considerable religious importance, they often have water springs, referred to as sacred. Some of such small settlements have grown increasingly popular with pilgrims and developed into quite sizeable towns. Consequently, the locations from which water is sampled had to be adapted to enable a larger number of people to draw – and often more – water in a shorter time. Because such water is regarded by pilgrims as possessing healing properties, it is usually drunk.

---

[1] Section of Limnology and Fishery, Wroclaw University of Environmental and Life Sciences, ul. J. Chełmońskiego 38C, 51–630 Wrocław, Poland, phone: +48 71 320 58 70, fax: +48 71 320 58 76, email: magdalena.senze@up.wroc.pl

Most probably a majority of the people using the water do not even think about its composition or any pollutants that may be present in it.

The tests were run in the years 2005–2008 on samples collected in south-eastern, central and western Europe: Gierzwald and Ludzmierz in Poland, Lourdes and La Salette in France, Fatima in Portugal and Ephesus in Turkey.

The aim of the research was to determine the pollution with heavy metals of waters sampled from the sacred springs in question.

Material and methods

The samples were collected into polyethylene bottles directly from the pipes from which water was taken by pilgrims. Immediately after they were collected measurements were taken of their reaction and electrolytic conductivity. Next they were mineralized in concentrated nitric acid. Metal (copper, zinc, lead, cadmium and nickel) concentrations were determined using atomic absorption spectrophotometry by means of a Varian Spectr AA-110/220 unit.

Results and discussion

The analysed waters were alkaline or slightly alkaline. The reaction values oscillated between 7.64 pH (Fatima) and 8.15 pH (Gierzwald) (Table 1). For none of the waters, apart from that from Gierzwald, for which the maximum was recorded, did the reaction exceed 8.00 pH. Under the Ordinance of 29 March 2007 of the Minister of Health, the reaction of water intended for human consumption should fall within the range 6.5–9.5 pH. This means that the waters in question satisfy the relevant requirements. According to the classification of surface waters intended for human consumption, the waters met the standards prescribed for category A1 on a three-level scale [1]. As per the guidelines regarding the presentation of the condition of groundwater, the waters met the cleanliness criteria for class 1 [2]. These alkaline waters could be help for example with hyperacidity (acid-alkaline balance).

Table 1

Reaction (pH) and electrolytic conductivity [$\mu S \cdot cm^{-1}$]

Site	Reaction (pH)	Electrolytic conductivity [$\mu S \cdot cm^{-1}$]
Gierzwald (Poland)	8.15	486.00
Ludzmierz (Poland)	7.72	365.00
Fatima (Portugal)	7.64	201.00
Ephesus (Greece)	7.73	702.00
Lourdes (France)	7.89	350.00
La Salette (France)	7.85	339.00

The results of the measurements of electrolytic conductivity were used to formulate conclusions about environmental pollution with mineral compounds. The lowest figure, at 201.00 μS · cm^{-1}, was obtained for the water collected at Fatima in Portugal (Table 1). The maximum was found at Ephesus (702.00 μS · cm^{-1}). The determined conductivity values fall, similarly to the reaction, within the limits set for water intended for human consumption (with the border value amounting to 2500 μS · cm^{-1}) [3]. In line with the guidelines for surface waters intended for human consumption, the waters from the sacred springs were identified as belonging to category A1 [1]. According to the groundwater classification, the waters in question met the requirements set for the best quality water class, except for the samples collected at Ephesus (702.00 μS · cm^{-1} – class II). The difference, however, is not significant, as the threshold value for class I amounts to 700 μS · cm^{-1} [2].

The analysis of heavy metal concentrations covered copper, zinc, cadmium, lead and nickel. The highest copper concentration was found in the Fatima spring (0.0052 mgCu · dm^{-3}) (Fig. 1). The values obtained for Ephesus were not much lower (0.0048 mgCu · dm^{-3}). The lowest copper concentration was in the samples from Ludzmierz in Poland (0.0001 mgCu · dm^{-3}). The cut-off value for water intended for human consumption is 2.00 mgCu · dm^{-3}, and so all of the samples met the criteria set in the Ordinance referred to above [3]. In terms of copper concentration in surface waters intended for human consumption the waters in question fell within the first, A1 category [1]. According to the groundwater classification system, copper concentrations satisfied the requirements set for class 1 water, the maximum threshold for which amounts to 0.0100 mgCu · dm^{-3} [2].

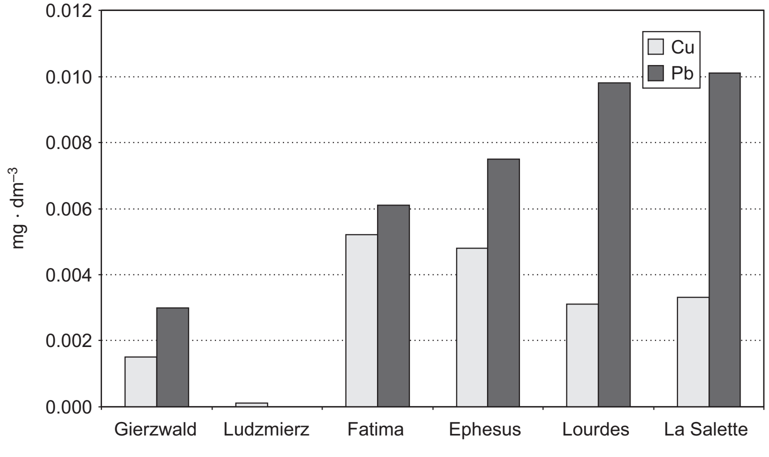

Fig. 1. Copper and lead in waters from sacred springs in Europe

Zinc content ranged from 0.0015 mgZn · dm^{-3} to 0.2153 mgZn · dm^{-3} (Fig. 2). The highest concentration was found in the case of water from Ephesus (Greece). Also the samples from Fatima had a high concentration of zinc, at 0.1115 mgZn · dm^{-3}. The lowest concentration was at Ludzmierz. The concentrations determined for Gierzwald and La Salette were similar, at 0.0300 mgZn · dm^{-3} and 0.0271 mgZn · dm^{-3}, respectively. The Ordinance of the Minister of Health referred to above does not

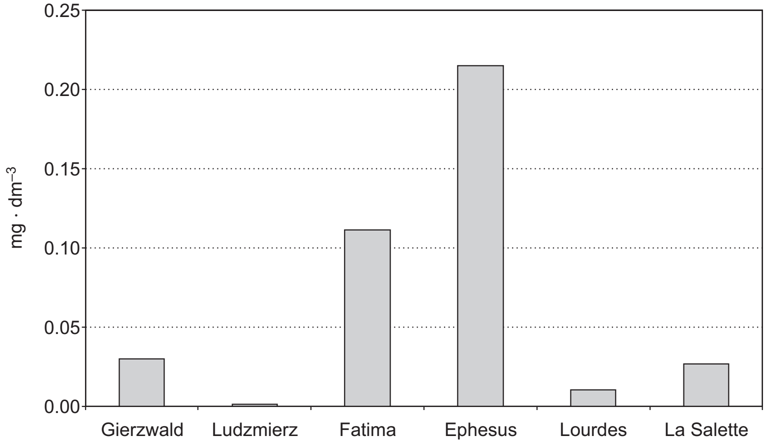

Fig. 2. Zinc in waters from sacred springs in Europe

regulate zinc content in potable water [3]. As per the groundwater classification system, the waters sampled in Poland (Gierzwald and Ludzmierz) and France (Lourdes and La Salette) belong to class 1, whereas those from Fatima and Ephesus – to class 2 [2]. According to the classification of surface waters intended for human consumption, all of the waters studied as part of the research met the requirements for the cleanest water category – A1 [1].

Cadmium concentrations proved the lowest at Ludzmierz (0.0005 mgCd · dm^{-3}) and the highest at Lourdes (0.0012 mgCd · dm^{-3}) (Fig. 3). The Gierzwald and Fatima samples had 0.0008 mgCd · dm^{-3}, and those from La Salette and Ephesus – 0.0009 mgCd · dm^{-3}. All of the samples fell within the range of values specified in the Ordinance of the Minister of Health referred to above, which sets the maximum

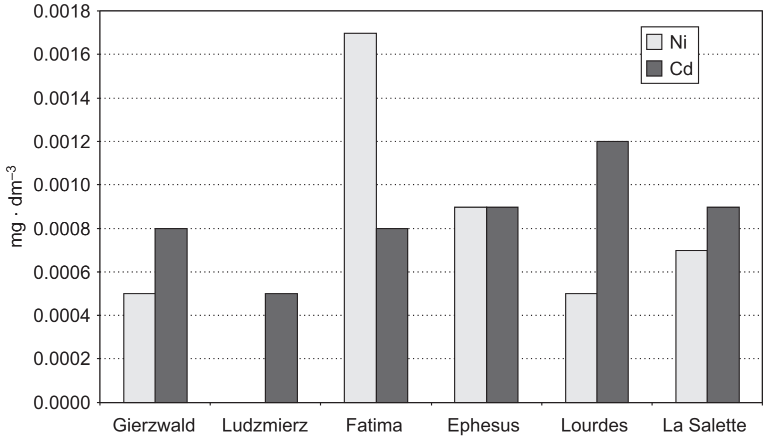

Fig. 3. Nickel and cadmium in waters from sacred springs in Europe

permissible concentration at 0.0050 mgCd · dm^{-3} [3]. According the surface water classification, the determined cadmium levels met the requirements for category A1 [1]. Under the groundwater classification system, the waters covered by the research belong to class 1, except for the water from Lourdes, which is class 2, with the maximum concentration threshold at 0.0010 mgCd · dm^{-3} [2].

As far as lead is concerned, its maximum concentration was found at La Salette (0.0101 mgPb · dm^{-3}) (Fig. 1). A lot of lead was also found in the water from Lourdes (0.0098 mgPb · dm^{-3}). No lead was found in the water samples from Ludzmierz. All the recorded values fall within the limits prescribed by the Ministry of Health [3]. Based on the recommendations of the Minister of the Environment regarding groundwater, all of the waters in question belong to the highest water cleanliness class [2]. The same applies to the classification of surface waters intended for human consumption (category A1) [1].

No nickel was found at Ludzmierz. The highest nickel concentration was at Fatima (0.0017 mgNi · dm^{-3}) (Fig. 3). The samples from Gierzwald and Lourdes had the same concentration of the metal: 0.0005 mgNi · dm^{-3}. The maximum permissible nickel concentration in water intended for human consumption amounts to 0.0200, and so all of the samples qualify as fit for consumption [3]. Nickel concentrations in the waters in question were low and so all of the waters belong to groundwater cleanliness class 1 and to category A1 for surface waters [1, 2].

Recapitulation

The tests showed that the waters in question, which are believed by pilgrims to possess medicinal and healing properties, met the criteria established for water intended for human consumption in terms of their the pH value, conductivity and heavy metal concentrations.

References

[1] Rozporządzenie Ministra Środowiska z dnia 27 listopada 2002 r. w sprawie wymagań, jakim powinny odpowiadać wody powierzchniowe wykorzystywane do zaopatrzenia ludności w wodę przeznaczoną do spożycia. DzU 2002, nr 204, poz. 1728.

[2] Rozporządzenie Ministra Środowiska z dnia 23 lipca 2008 r. w sprawie kryteriów i sposobu oceny stanu wód podziemnych. DzU 2008, nr 143, poz. 896.

[3] Rozporządzenie Ministra Zdrowia z dnia 29 marca 2007 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi. DzU 2007, nr 61, poz. 417.

OBECNOŚĆ METALI W WODACH ZE ŚWIĘTYCH ŹRÓDEŁ W EUROPIE

Zakład Hydrobiologii i Akwakultury
Uniwersytet Przyrodniczy we Wrocławiu

Abstrakt: Przeprowadzono badania wód pochodzących ze źródeł w zlokalizowanych w miejscowościach na terenie Europy: w Polsce (Gierzwałd i Ludźmierz), we Francji (Lourdes, La Salette), w Portugalii (Fatima) oraz w Grecji (Efez). Określono odczyn, konduktywność (przewodnictwo elektrolityczne) oraz stężenia:

miedzi, cynku, kadmu, ołowiu i niklu. Badane wody odznaczały się odczynem w zakresie od 7,64 pH do 8,15 pH. Konduktywność wahała się od 201,00 do 702,00 $\mu S \cdot cm^{-1}$. Zakresy zawartości metali wynosiły dla miedzi (0,0001–0,0052 $mgCu \cdot dm^{-3}$), dla cynku (0,0015–0,2153 $mgZn \cdot dm^{-3}$), dla kadmu (0,0005–0,0012 $mgCd \cdot dm^{-3}$), dla ołowiu (0,0000–0,0101 $mgPb \cdot dm^{-3}$) oraz dla niklu (0,0000–0,0017 $mgNi \cdot dm^{-3}$). Na podstawie przeprowadzonych badań okazało się, że badane wody, które uznawane są przez pielgrzymów jako mające właściwości lecznicze i uzdrawiające, spełniają kryteria ustalone dla jakości wód przeznaczonej do spożycia dla ludności.

Słowa kluczowe: woda, metale, święte źródła

DOI: 10.2428/ecea.2012.19(01)014 ECOL CHEM ENG A. 2012;19(1-2):129-136

Urszula PANKIEWICZ[1]

MONITORING OF TOTAL MERCURY LEVEL IN SELECTED DAIRY PRODUCTS FROM THE SOUTH-EAST REGIONS OF POLAND

MONITORING POZIOMU RTĘCI CAŁKOWITEJ W WYBRANYCH PRODUKTACH MLECZARSKICH Z REGIONÓW POŁUDNIOWO-WSCHODNIEJ POLSKI

Abstract: Mercury content was examined in forty-eight milk products produced by *regional milk cooperatives* (OSM) located in south and south-east Poland. In the market range of products, the mercury content was lower than the permissible level of 10 μg/kg. The lowest mercury concentration, 0.01 μg/kg of product, was determined in kefir and the highest one – in milk and it was equal 0.79 μg/kg of product. The examined products are not dangerous for the consumers because the mercury content do not exceed a boundary value recommended by FAO/WHO. They also do not point at any pollution of natural or agricultural areas by this toxic element.

Keywords: mercury content, milk products, non-flame atomic spectrometry absorption technique

One percent of the global emission of mercury, that is about 20 Mg (ton)/year, falls on Poland. It put our country on the second place in the EU ranking [1]. Growing environmental pollution caused consumers' fears of consumption of products containing heavy metals. These metals get inside the human body mainly by inhalation and consumption and then cumulate. Usually their toxic action do not appear at once, but after many years or even in the next generations. Heavy metals present in food even in trace amounts are very dangerous for the human health, because they cause non-infectious diseases which are characterized by the far effects of action. Polish legal acta, based on EU directives, permits the following mercury contents in foodstuff: 0.01 mg/kg in milk; 0.01 mg/kg in fruits, vegetables, leguminous vegetables, potatoes; 0.02 mg/kg in oil seeds, tea, hop; and 0.01 mg/kg in other foodstuffs of plant origin.

---

[1] Department of Analysis and Evaluation of Food Quality, Faculty of Food Science and Biotechnology, University of Life Sciences in Lublin, ul. Skromna 8; 20–704 Lublin, Poland, phone: +48 81 462 33 33, fax: +48 81 462 33 76, email: urszula.pankiewicz@up.lublin.pl

Mercury occurs in several chemical forms including elemental mercury, as well as its inorganic and organic compounds [2], which differ in their solubility, reactivity and toxicity [3]. Global mercury circulation involves both natural and anthropogenic sources [4]. The main source of mercury is natural emission originating from volcanic eruptions and evaporation from the ocean and land surfaces. Mercury poisoning caused by mercury vapour and inorganic compounds of this element are mainly connected with the development of industry, while methylmercury (MeHg) is a serious environmental pollutant [5, 6]. It is reported that limited amounts of inorganic and organic mercury can be passed from feed to cow's milk [7, 8] and cumulate in dairy products. Therefore, monitoring of mercury presence in such products is so important [9].

The aim of this work was analysis of mercury content in milk and dairy products originated from south and south-eastern Poland.

Materials and methods

Milk and a range of dairy products originated from south and south-east regions of Poland were purchased from the local markets. The main criterion was the selection of producers from the regions differing in their degree of industrialization and, consequently, pollution of the environment. Mercury content was analyzed in the products such as: milk, buttermilk, kefir, yogurt, cream, cream cheese, cottage cheese, butter and milk powder in order to asses if degree of concentration of a raw material and food processing have an influence on its level in dairy products.

Measurement of water content. Water content of liophilizates and products was determined with the use of a moisture analyzer (Radwag WPS50SW) after drying samples at 100 ^{o}C. Analysis was carried out in triplicate.

Lyophilization. Samples of dairy products were lyophilized in Labconco freeze dryer (Model 64132, Kansas City, MO, USA). Obtained lyophilizates were stored in an exsiccator and used for the further analyses.

Determination of total mercury content. Mercury content in such prepared lyophilized samples was specified using non-flame atomic spectrometry absorption technique (mercury analyzer AMA 254, Altec, Czech Republic). During the analysis in the AMA 254, samples were pre-dried in the internal oven of the analyzer and burned in oxygen (99.999 % of purity). The decomposition products were further carried to the amalgamator for selective mercury trap. After temperature stabilization (120 ^{o}C) in the amalgamator the content of trapped mercury was measured. Thus mercury was released from the amalgamator by a short heat-up and then the mercury cloud was transferred by O_2 carrier gas to a double measuring cuvette. Then the same quantity of mercury was measured twice using different sensitivities, resulting in a dynamic range of 0.05–600 ng Hg in single measurement. The detection limit was 10^{-5} μg/g. The original factory calibration was still valid for the calibration of the instrument. The values were controlled regularly by calibration standard mercury solutions – NIST- traceable Hg standard solution (Accu Trace Single Element Standard; AccuStandard Inc., New Haven, Ct, USA). Each sample was analyzed in triplicate and the data are an average of these replications. Additionally, *standard deviation* (SD) for each determination was calculated. Mercury content in lyophilizate was converted to its concentration in the base product.

Results and discussion

Mean values of mercury content [μg/kg] determined in lyophilizates and base products are presented in Table 1. Mercury levels in all the examined products were in the order of ten thousandth parts of ppm and oscillated from about 0.01 μg/kg in natural kefir (7D, 6C), cream (5D), buttermilk (5C) and strawberry flavoured yogurt “Serduszko” (3D) to over 0.45 μg/kg in butter from all the producers – the highest value determined for butter 10A was equal 0.79 μg/kg.

Variety of mercury content was observed among the products originated from the same dairy or region of Poland:

– OSM (A) – from 0.00002 ppm in kefir (2A) to 0.00030 ppm in milk powder (8A) and 0.00079 ppm in butter extra (10A);

– OSM (B) – from 0.00003 ppm in milk (1B) to 0.00010 ppm in half fat cottage cheese (8B);

– OSM (C) – from 0.00001 ppm in kefir (6C) and buttermilk (5C) to 0.00014 ppm in vanilla flavoured cream cheese (2C) and 0.00058 ppm in butter extra (10C);

– OSM (D) – from 0.00001 ppm in natural kefir (7D), cream (5D) and strawberry flavoured yogurt (3D) to 0.00011 ppm in vanilla flavoured cream cheese (8D);

– OSM (E) – from 0.00004 ppm in kefir (5E) to 0.00016 ppm in cream cheese with spring onion (4E);

– OSM (F) – from 0.00002 ppm in kefir (2F) to 0.00008 ppm in granular cottage cheese (3F) and 0.00047 ppm in butter extra (5F).

To summarize, if a certain dairy produced kefir, it contained the lowest mercury level from the whole range of products. The highest mercury content was determined in butter in the case of all the producers.

Some differences in mercury content were observed in the particular range of dairy products (Table 1). Similar products originated from the different regions of Poland revealed diversity in mercury content (Table 1), for instance milk contained from *ca* 0.03 μg Hg/kg (OSM B from Silesia) to 0.06 μg Hg/kg (OSMs A and F from Lublin and Podkarpackie provinces).

The lowest amounts of mercury in the whole range of dairy products were determined for kefirs – from 0.01 μg Hg/kg (OSMs D and C) to 0.04 μg Hg/kg (OSM E). For kefirs produced by OSMs A and F, mercury content was about 0.02 μg/kg (Table 1).

Similar mercury concentrations, in the range of 0.01–0.09 μg/kg, were obtained for buttermilks, yogurts and creams. Among buttermilks, that produced by OSM C contained the highest amount of mercury and the lowest value was obtained for buttermilk produced by OSM A.

Strawberry flavoured yogurt produced by OSM D contained the lowest amount of Hg in the examined range of products, whereas the highest mercury content was obtained for natural yogurt of OSM C. Addition of flavour supplements or fruits to yogurt did not cause any increase of mercury content.

Table 1

Mercury content in dairy products and their lyophilizates.
A, B, C, D, E, F – codes of the particular producers

No.	Code	Product	Hg content in lyophylizate (mean ± SD) [μg/kg]	Hg content in product (mean ± SD) [μg/kg]
1	1A	Milk	0.53 ± 0.07	0.06 ± 0.01
2	2A	Kefir	0.11 ± 0.05	0.02 ± 0.01
3	3A	Natural yogurt	0.17 ± 0.02	0.03 ± 0.00
4	4A	Natural yogurt “JOGUŚ”	0.32 ± 0.07	0.05 ± 0.01
5	5A	Cream	0.23 ± 0.09	0.06 ± 0.02
6	6A	Cream cheese (vanilla taste)	0.37 ± 0.01	0.12 ± 0.00
7	7A	Half fat cottage cheese	0.77 ± 0.02	0.23 ± 0.01
8	8A	Whole milk powder	0.31 ± 0.02	0.30 ± 0.01
9	9A	Buttermilk	0.11 ± 0.04	0.09 ± 0.03
10	10A	Butter extra	0.90 ± 0.90	0.79 ± 0.79
11	1B	Milk	0.24 ± 0.07	0.03 ± 0.01
12	2B	Vanilla flavoured cream cheese	0.12 ± 0.05	0.05 ± 0.02
13	3B	Natural cream cheese	0.27 ± 0.04	0.05 ± 0.01
14	4B	Cream	0.19 ± 0.04	0.04 ± 0.01
15	5B	Cream cheese with horseradish	0.30 ± 0.12	0.09 ± 0.04
16	6B	Cream cheese with caraway	0.14 ± 0.05	0.06 ± 0.02
17	7B	Natural buttermilk	0.49 ± 0.04	0.06 ± 0.01
18	8B	Half fat cottage cheese	0.32 ± 0.04	0.10 ± 0.01
19	1C	Natural yogurt “Nadburzański”	0.38 ± 0.08	0.07 ± 0.02
20	2C	Vanilla flavoured cream cheese	0.45 ± 0.04	0.14 ± 0.01
21	3C	Natural cream cheese	0.22 ± 0.06	0.05 ± 0.01
22	4C	Natural yogurt	0.25 ± 0.02	0.03 ± 0.00
23	5C	Buttermilk	0.13 ± 0.06	0.01 ± 0.01
24	6C	Kefir	0.08 ± 0.08	0.01 ± 0.01
25	7C	Cream	0.17 ± 0.11	0.03 ± 0.02
26	8C	Milk “Nadbużański dzban”	0.25 ± 0.16	0.03 ± 0.02
27	9C	Half fat cottage cheese	0.13 ± 0.03	0.04 ± 0.01
28	10C	Butter extra	0.65 ± 0.29	0.58 ± 0.26
29	1D	Vanilla flavoured cream cheese “Serduszko”	0.18 ± 0.10	0.04 ± 0.02
30	2D	Yogurt “Regularis”	0.23 ± 0.15	0.06 ± 0.04
31	3D	Strawberry flavoured yogurt “Serduszko”	0.12 ± 0.06	0.01 ± 0.01
32	4D	TZATZIKI with fresh cucumber and garlic	0.11 ± 0.05	0.02 ± 0.01
33	5D	Cream	0.05 ± 0.04	0.01 ± 0.01
34	6D	Natural yogurt	0.28 ± 0.17	0.04 ± 0.02

Table 1 contd.

No.	Code	Product	Hg content in lyophylizate (mean ± SD) [μg/kg]	Hg content in product (mean ± SD) [μg/kg]
35	7D	Natural kefir	0.08 ± 0.03	0.01 ± 0.00
36	8D	Vanilla flavoured cream cheese	0.14 ± 0.06	0.11 ± 0.05
37	1E	Cream	0.22 ± 0.20	0.05 ± 0.04
38	2E	Natural cottage cheese	0.51 ± 0.07	0.12 ± 0.02
39	3E	Natural cottage cheese “Domowy”	0.38 ± 0.08	0.08 ± 0.02
40	4E	Cream cheese with spring onion “Twój smak”	0.44 ± 0.12	0.16 ± 0.04
41	5E	Kefir	0.29 ± 0.15	0.04 ± 0.02
42	6E	Half fat cottage cheese	0.18 ± 0.09	0.13 ± 0.07
43	1F	Cream	0.13 ± 0.02	0.03 ± 0.01
44	2F	Kefir	0.23 ± 0.13	0.02 ± 0.01
45	3F	Granular cottage cheese	0.32 ± 0.13	0.08 ± 0.03
46	4F	Half fat cottage cheese KRAJANKA	0.19 ± 0.10	0.05 ± 0.03
47	5F	Butter extra	0.55 ± 0.19	0.47 ± 0.16
48	6F	Milk	0.60 ± 0.19	0.06 ± 0.02

Mean – mean arithmetic value; SD – standard deviation.

Among examined creams, that produced by OSM D was characterized by the lowest content of mercury and the highest content of this element was obtained for cream of OSM A (Table 1). Slightly higher amounts of mercury were determined in the case of cream cheeses and cottage cheeses. Natural cream cheeses (3B and 3C) and vanilla flavoured cream cheese (2B) contained the lowest amount of mercury – 0.05 μg/kg. Cream cheese with spring onion (OSM E) was characterized by the highest mercury content – 0.16 μg/kg (Table 1). Cottage cheeses from the different regions of Poland contained various amounts of mercury – from 0.04 and 0.05 μg /kg in the case of half fat cottage cheese of OSMs C and F, respectively, to 0.23 μg /kg for cottage cheese produced by OSM A. Half fat cottage cheese from Silesia and cottage cheese produced by OSM E contained a moderate mercury level of, respectively, 0.10 and 0.13 μg/kg of product (Table 1).

The highest level of mercury in the whole range of dairy products was obtained for butter originated from different parts of Poland. This level was as high as 0.79 μg Hg/kg of product in the case of butter extra produced by OSM A. The lower contents, respectively, 0.33 do 0.50 μg Hg/kg, were noted for butter extra from OSM F and OSM C (Table 1).

The investigations allowed to asses how environmental pollution and concentration of component in technological processes influence mercury content in dairy products representing a wide range of assortment and originated from various regions of the country. Mercury concentration varied from 0.01 to 0.79 μg/kg, which means that the lowest concentration corresponds with a detection limit of the apparatus.

Taking into consideration the mean contents of mercury in all the products of the particular producers, with the exception of butter and whole milk powder, there were no significant difference between them. What is interesting, the products from the less industrialized regions contained higher mean concentrations of mercury than those from the regions of higher environmental pollution. Mercury can be transferred over long distances to regions where there are no significant sources of emission.

In the year 2000, participation of the particular industrial sources in mercury emission to the air was as follows: power stations – 26.5 %, individual home fireplaces – 20.4 %, cement production – 12.6 %, chlorine production – 16.9 % (technology withdrawn from UE since 2007), ferrous metallurgy – 5.2 %, zinc and lead metallurgy – 6.5 %, oil burning – 0.7 %, waste burning – 4.8 %, other – 6.4 % (*ie* crematories) [10].

In the particular groups of assortment, big differences in mercury content were observed between butter as well as whole milk powder and the other products. Milk, cream and fermented milk drinks were characterized by the low values of mean mercury concentration and the lowest value – 0.02 μg Hg/kg, was noted for kefir. Safety of these product for the consumers' health is very important as they are valuable source of calcium in diet.

A small increase in mean mercury content (to 0.11 μg Hg/kg) was observed in the case of cream and cottage cheeses. Similar interactions were reported by Anastasio et al [11] who noted the highest mercury concentration in fresh sheep cheeses.

According to JECFA (*The Joint FAO/WHO Expert Committee on Food Additives*), *the provisional tolerable weekly intake* (PTWI) for mercury from all the sources is 0.005 mg/kg of body weight including 0.0016 mg/kg for organic mercury compounds. These values are continuously verified [12, 13].

European Commission Regulation (EC) No. 1881/2006 of 19 December 2006 [14] setting maximum levels for certain contaminants in foodstuffs, defines the limits of mercury concentration exclusively in fish and seafood – 0.5 mg Hg/kg of wet weight (for the chosen fish species – 1.0 mg/kg). The research concerning mercury content in various foodstuffs, carried out in recent years showed that they are not dangerous for human's health. For the particular assortments of food concentrates, values of mercury concentration were as follows:

– desserts, ersatz coffee, juices and beverages – 0.001 mg/kg (0.001 ppm),

– ice-creams, broths and protein hydrolysates – 0.002 mg/kg (0.002 ppm),

– instant soups – 0.013 mg/kg (0.013 ppm), especially high mercury content was determined in boletus soup, champignon soup and cream soup and beetroot soup [12].

Analysis of bakery and confectionery flours revealed that mercury concentration was lower than 0.1 mg/kg, whereas the *maximum permissible* dose is equal 0.2 mg/kg [15]. In 2004 the monitoring research of mercury content in foodstuffs was carried out and the results were as follows: wheat and mixed bread, flours, grouts and noodles – 0.003 mg/kg; confectionery products – 0.002 mg/kg; food for infants and young children (dairy, cereal, vegetable and soy products) – 0.002 mg/kg [16]. On the other hand, herbal products contained less than 0.01 mg Hg/kg and only in one case mercury content was slightly higher than 0.02 mg/kg [17]. Results of the studies concerning mercury content in milk and dairy products, obtained in different countries and in different years, are presented below:

- Roh et al 1975 (Korea) [18] – 3–10 ppb,
- Sell et al 1975 (North Dacota) [19] – less than 2 ppb,
- Sell and Davison 1975 (North Dacota) [20] – less than 1 ppb,
- Dobrzanski et al 2009 (Poland, Wroclaw) [21] – 0.24 and 0.27 ppb,
- Silesia (late 80s.) – 0.3–6.7 ppb,
- region of Zgorzelec and Bogatynia – 2 ppb,
- Spain, the Canary Islands – 0.09–0.61 ppb,
- China – 1.0–3.9 ppb,
- Italy, Rome surroundings – 0.9–38 ppb,
- Egypt – even 86–556 ppb [21].

The national norms specify the maximum mercury content in food which is various, depending on the country, *eg* 1 mg Hg/kg in Sweden and Japan, 1.5 mg Hg/kg in Norway and 0.5 mg Hg/kg in Poland. In the latter country, the maximum concentration of mercury in milk has been officially established at 10 μg/kg (10 ppb) [21]. Comparing the results obtained for the examined products with above-mentioned data, it can be observed that they are lower and do not exceed permissible levels. Therefore, it can be assumed, that the investigated dairy products do not pose a threat to consumers' health and can be safely consumed providing valuable nutrients.

Conclusions

In all studied dairy products the mercury content was lower than the permissible level of 10 μg/kg. Results indicate no hazard of mercury intoxication when using dairy products of Polish production.

References

[1] Komosa A, Kitowski I, Kowalski R, Pitucha G, Komosa Z, Grochowicz J. Total mercury concentration in kidneys of birds of prey from different part of Poland – Some interspecies and geographical differences. Ecol Chem Eng S. 2009;16(1):19-28.

[2] Davidson PW, Myers GJ, Weiss B. Mercury exposure and child development outcomes. Pediatrics. 2004;113:1023-1029.

[3] Goldman LR, Shannon MW. The Committee on Environmental Health: Technical Report: Mercury in the Environment: Implications for Pediatricians. Pediatrics. 2001;108(1):197-205.

[4] Myers GJ, Davidson PW. Does methylmercury have a role in causing developmental disabilities in children? Environ Health Persp. 2000;108(3):413-420.

[5] Langauer-Lewowicka H. Neurotoksyczność rtęci metalicznej – trudności diagnostyczne. Med Pr. 2003;54(4):377-382.

[6] Orłowski Cz. Metale. In: Piotrowski JK, editor. Podstawy toksykologii. Kompendium dla studentów szkół wyższych. Wydanie II. Warszawa: WNT; 2008.

[7] Neathery MW, Miller WJ, Gentry RP, Stake PE, Blackmon D. Cadmium-109 and methyl mercury-203 metabolism, tissue distribution, and secretion into milk of cows. J Dairy Sci. 1974;57(10):1177-1183.

[8] Neathery MW, Miller WJ. Metabolism and toxicity of cadmium, mercury, and lead in animals. J Dairy Sci. 1975;58(12):1767-1781.

[9] Cava-Montesinos P, Rodenas-Torralba E, Morale-Rubio A, Cervera ML, De La Guardia M. Cold vapour atomic fluorescence determination of mercury in milk by slurry sampling using multicommutation. Anal Chim Acta. 2004;506:145-153.
[10] Borodeńko A, Prokopowicz A. Stężenie par rtęci w powietrzu w Katowicach. Zesz Nauk Wyż Szkoły Zarządzania Ochroną Pracy w Katowicach, 2007;1:23-30.
[11] Anastasio A, Caggiano R, Macchiato M, Paolo C, Ragosta M, Paino S, Cortesi ML. Heavy metal concentrations in dairy products from sheep milk collected in two regions of southern Italy. Acta Vet Scand. 2006;47(1):69-74.
[12] Mania M, Wojciechowska-Mazurek M, Starska K, Karłowski K. Koncentraty spożywcze – zanieczyszczenie pierwiastkami szkodliwymi dla zdrowia. Bromat Chem Toksykol. 2009;42(3):448-454.
[13] Wojciechowska-Mazurek M, Starska K, Brulińska-Ostrowska E, Plewa M, Biernat U, Karłowski K. Monitoring zanieczyszczenia żywności pierwiastkami szkodliwymi dla zdrowia. Część I. Produkty zbożowe pszenne, warzywne, cukiernicze oraz produkty dla niemowląt i dzieci (rok 2004). Roczn PZH. 2008;59:251-266,.
[14] Rozporządzenie Komisji (WE) Nr 1881/2006 z dnia 19 grudnia 2006 r. ustalające najwyższe dopuszczalne poziomy niektórych zanieczyszczeń w środkach spożywczych.
[15] Cichoń Z, Ptak M. Analiza jakości wybranych rodzajów mąki pszennej. Zesz Nauk Akad Ekonom w Krakowie. 2005;678:89-102.
[16] Farid SM, Enani MA, Wajid S.A. Determination of trace elements in cow's milk in Saudi Arabia. J King Abdulaziz Univ: Eng Sci. 2004;15(2):131-140.
[17] Kowalski R, Kucharski A. Monitoring of total mercury level in selected herbal products. Herba Pol. 2007;53(3):235-240.
[18] Roh JK, Bradley RLJ, Richardson T, WeckeL KG. Distribution and removal of added mercury in milk. J Dairy Sci. 1975;58(12):1782-1788.
[19] Sell JL, Deitz FD, Buchanan ML. Concentration of mercury in animal products and soils of North Dakota. Arch Environ Con Toxicol. 1975;3:278-288.
[20] Sell JL, Davison KL. Metabolism of mercury, administered as methylmercuric chloride or mercuric chloride, by Lactating Ruminants. J Agric Food Chem. 1975;23:803-808.
[21] Dobrzański Z, Szulc T, Kupczyński R, Kuczaj M. Study on a content of mercury in hair, milk and blood of cows housed in an urbanized area. EJPAU. 2009;12.
on-line: http://www.ejpau.media.pl/volume12/issue2/art-02.html, April 2010.

MONITORING POZIOMU RTĘCI CAŁKOWITEJ W WYBRANYCH PRODUKTACH MLECZARSKICH Z REGIONÓW POŁUDNIOWO-WSCHODNIEJ POLSKI

Katedra Analizy i Oceny Jakości Żywności
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: Celem pracy było określenie poziomu stężenia rtęci całkowitej w mleku i produktach mleczarskich pochodzących z rejonów południowo-wschodniej Polski. Oznaczanie prowadzono z użyciem analizatora rtęci AMA-254. W pracy przebadano 48 produktów, począwszy od mleka spożywczego, a skończywszy na mleku w proszku, co miało na celu określenie wpływu koncentracji surowca na ewentualny wzrost stężenia rtęci w próbkach. Zawartość rtęci w badanych produktach mleczarskich nie przekracza dopuszczalnego limitu stężenia rtęci w mleku, jako produkcie spożywczym, który wynosi 10 μg/kg (10 ppb). Najmniej rtęci zawierają kefiry (0.01 μg Hg/kg produktu, Biomlek), natomiast największa jej ilość występuje w masłach (0.79 μg Hg/kg produktu, Krasnystaw). W świetle obecnego stanu wiedzy analizowane produkty nie stanowią zagrożenia dla konsumentów, jeśli chodzi o skażenie rtęcią. Uzyskane dane wskazują, że produkty mleczarskie pochodzące z Polski południowo-wschodniej nie dają jakichkolwiek niepokojących przesłanek informujących pośrednio o ewentualnym skażeniu terenów naturalnych czy rolniczych tym toksycznym pierwiastkiem.

Słowa kluczowe: rtęć, produkty mleczarskie, bezpłomieniowa absorpcyjna spektrometria atomowa

DOI: 10.2428/ecea.2012.19(01)015 ECOL CHEM ENG A. 2012;19(1-2):137-144

Sebastian WERLE[1]

ANALYSIS OF THE POSSIBILITY OF THE SEWAGE SLUDGE THERMAL TREATMENT

ANALIZA MOŻLIWOŚCI ENERGETYCZNEGO WYKORZYSTANIA OSADÓW ŚCIEKOWYCH

Abstract: Promoting of the renewable energy is one of the priorities of the Polish energy policy until the year of 2030. It is believed that the co-combustion of sewage sludge in the Polish conditions is especially attractive. The paper contains two parts of research. The first one concerns a theoretical analysis of the possibility of direct co-combustion of solid municipal sewage sludge with hard coal in power station boilers. Numerical simulation of indirect co-combustion process of gas from sewage sludge gasification in coal-fired boiler has been done in the second part of the work. The conclusions show that the thermal methods of sewage sludge utilisations provide a great opportunity for application in Polish conditions.

Keywords: direct co-combustion, indirect co-combustion, sewage sludge

According the Polish Regulation and the objectives of the National Waste Management Plan 2014 [1] and the National Urban Wastewater Treatment Program [2] the quantity of sewage treated in Poland is systematically increasing. Currently, the predominant method for the disposal of sewage sludge is its storage and agricultural application [3]. The main problems are the high percentage of stored sewage sludge and a lack of installations for its thermal utilization. Thermal processes can be used for the conversion of large quantities of sewage sludge (*eg*, in large urban areas) into useful energy. There is a wide range of analysed and proposed solutions for municipal sewage sludge utilization. Nevertheless, there are serious legal constraints determining this choice. One of the most important Regulation is the Regulation of the Minister of Economy and Labour [4], which introduced a ban of the storage of sewage sludge from the date of January 1, 2013.

In view of the presented facts, there is a large and pressing need for the development of thermal methods (combustion, co-combustion, gasification and pyrolysis) of disposal of sludge.

---

[1] Institute of Thermal Technology, Silesian University of Technology, ul. Konarskiego 22, 44–100 Gliwice, Poland, phone: +48 32 237 29 83, email: sebastian.werle@polsl.pl

Taking into consideration Polish specificity of the power engineering sector which is based on the coal-fired boilers, the most promising method of sewage sludge treatment in Poland is co-combustion. Basically, it is mainly possible to distinguish the use of sewage sludge in fossil fired power plants in two different co-combustion concepts, which are as follows:

1. Direct co-combustion (Fig. 1): Sewage sludge and coal are burned in the same boiler or gasifier, using the same or separate mills and burners, depending principally on the sewage sludge fuel characteristics. Coal and sludge can be mixed before milling or coal and sludge are fed and milled by separated supply chains.

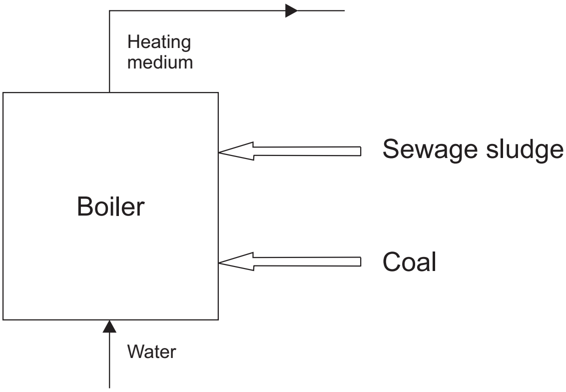

Fig. 1. Scheme of direct co-combustion idea

2. Indirect co-combustion (Fig. 2): In gasifier sewage sludge is converted into a fuel gas, which after cooling and cleaning can be burned in the coal boiler furnace. As an alternative the produced syngas can also directly be burnt in a joint steam boiler without further cooling or cleaning.

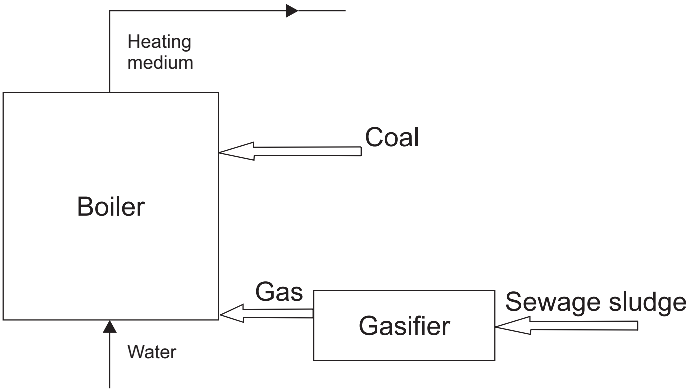

Fig. 2. Scheme of indirect co-combustion idea

The aim of the work is – first of all – theoretical analysis of the possibility of direct co-combustion of solid municipal sewage sludge with hard coal in power station boilers (WR-25, CFB-420 and OP-230) and – secondly – numerical simulation of indirect co-combustion process of gas from sewage sludge gasification in coal-fired boiler.

Materials and methods

First part of the present work [5] consists theoretical analysis of the possibility of the direct co-combustion of dried sewage sludge in different types of the coal-fired boilers (fluidized bed boiler CFB-420, stoker fired boiler WR-25 and pulverized coal boiler OP-230). Main boilers parameters are presented in Table 1.

Table 1

Main parameters of analyzed boilers [6]

	WR-25	CFB-420	OP-230
Nominal boiler efficiency [%]	82.0	90.7	89.0
Flue gas temperature [^{o}C]	180.0	128.0	150.0
Water temperature on inlet [^{o}C]	70.0	230.0	200.0
Heating medium temperature on outlet [^{o}C]	150.0	538.0	540.0

The analysis takes into consideration wide range of mass fraction of sewage sludge (0–20 %) in the fuel (hard coal) mixture and wide range of air excess ratio in the combustion chamber (1.1–1.5). Boiler efficiency in all analysed examples was calculated. Energy balance of all analysed boilers was done. Composition of the analysed fuels blends are presented in Table 2.

Table 2

Composition of the analyzed fuels

Mass fraction of main components in mixture	Mass fraction of sewage sludge in fuel mixture [%]				
	0	5	10	15	20
C	0.6867	0.6542	0.6246	0.5977	0.5730
H	0.0083	0.0087	0.0091	0.0094	0.0097
S	0.0466	0.0468	0.0469	0.0470	0.0472
O	0.0849	0.0932	0.1070	0.1076	0.1141
N	0.0178	0.0205	0.0230	0.0252	0.0272
H_2O	0.0493	0.0517	0.0539	0.0559	0.0577

Equilibrium calculations of coal-sewage sludge mixtures complete combustion in analysed boilers were done. Energy balance illustration is presented in Fig. 3.

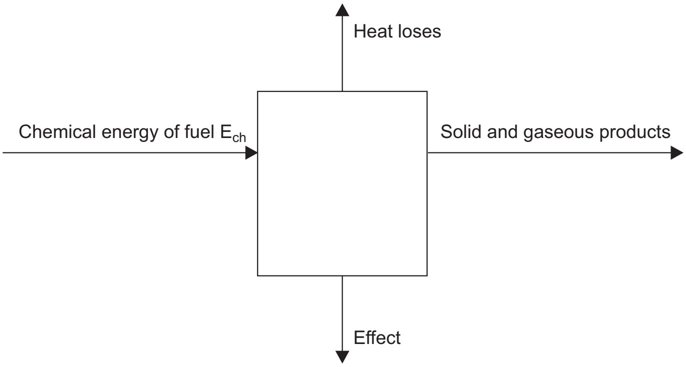

Fig. 3. Illustration of energy balance

Energy balance solution using real operating parameters of all analysed boilers (capacity, operating temperatures and pressures etc.) leads to determination of the flow of combusted fuel $\dot{P}$. Thanks to it, boilers efficiency using eq. (1) can be determined:

$$\eta = \frac{Effect}{E_{ch}} = \frac{\dot{Q}}{\dot{P} \cdot W_d} \tag{1}$$

where: $\dot{Q}$ – boiler capacity [kW];
$\dot{P}$ – flow of the fuel [kg/s];
W_d – lower heating value [kJ/kg].

In the second part of the work, numerical simulation of the indirect co-combustion of sewage sludge gasification gas in coal-fired boiler, NO_x reduction efficiency has been calculated. The calculations were modelled using the GRI-Mech 2.11 mechanism. This version is used for analysing the reburning process. The molar flow rate ratio of the reburning fuel to the whole exhaust was assumed to be 5 %, 10 % and 15 %. The simulations were conducted at a constant pressure equal to 1 atm and at temperatures ranging from 600 to 1400 ^{o}C, with typical residence times of 0.0–0.4 s [7] and local air excess ratio ranging from 1.0 to 2.0. The *local air excess ratio* in this paper is defined as the weight ratio of air to unreacted fuel used in the entrance of the reduction zone divided by the fuel ratio for stoichiometric combustion [8].

The residence time of the reactants in the reburning zone is a very important factor. In a real boiler, the residence time includes the mixing time between the products coming from the primary zone and the reburning fuel, and the reaction time of those products. It was assumed that all reactants enter the reactor already premixed, so the residence time is taken as the reaction time. It was assumed that the flue gases entering the reburning zone contain 300 ppm NO and that during combustion only NO is formed without other NO_x.

Results and discussion

Direct co-combustion

The calculated values of boiler efficiency are presented in Table 3. Analyzing those results it can be concluded that, taking into consideration constant value of boiler capacity, both increasing of mass fraction of sewage sludge in fuel mixture and increasing of air excess ratio causes decreasing of boiler efficiency. Nevertheless, it should be emphasis that this decrement is not very high and mainly causes by high value of exhaust loss. It can be concluded, that direct co-combustion of sewage sludge in different types of coal-fired boilers does not negatively affect on boiler efficiency.

Table 3

Efficiency of analysed boilers

λ	WR-25					CFB-420					OP-230				
	Mass fraction of sewage sludge in fuel mixture [%]														
	0	5	10	15	20	0	5	10	15	20	0	5	10	15	20
1.10	**90.8**	90.8	90.7	90.7	90.6	92.6	92.5	92.5	92.5	92.4	**82.7**	82.6	82.5	82.4	82.3
1.15	90.5	90.5	90.4	90.4	90.4	92.3	92.3	92.3	92.2	92.2	82.0	82.0	81.8	81.8	81.7
1.20	90.2	90.2	90.1	90.1	90.1	92.1	92.1	92.0	92.0	92.0	81.4	81.3	81.2	81.2	81.1
1.25	90.0	89.9	89.9	89.8	89.8	91.9	91.9	91.8	91.8	91.8	80.8	80.7	80.6	80.5	80.4
1.30	89.7	89.6	89.6	89.6	89.5	91.7	91.6	91.6	91.6	91.5	80.2	80.1	80.0	79.9	79.8
1.35	89.4	89.4	89.3	89.3	89.2	91.5	91.4	91.4	91.4	91.3	79.6	79.5	79.4	79.3	79.2
1.40	89.1	89.1	89.0	89.0	89.0	91.2	91.2	91.2	91.1	91.1	79.0	78.9	78.7	78.7	78.6
1.45	88.9	88.8	88.8	88.7	88.7	91.0	91.0	90.9	90.9	90.9	78.3	78.2	78.1	78.0	78.0
1.50	88.6	88.5	88.5	88.4	**88.4**	90.8	90.8	90.7	90.7	90.6	77.7	77.6	77.5	77.4	**77.3**

Indirect co-combustion

In Fig. 4, relative amount of NO_x as a function of temperature is shown. NO reduction efficiency of the gasification gas is strongly dependent on temperature. Temperature in the additional fuel injection zone is a key variable in the process because it determines the degree of conversion of the additional fuel and thus the formation of hydrocarbon radicals, as well as the rates of important reactions involved in the reburning mechanism. The reduction of NO increases with increasing temperature – presumably through its reaction with CH_i – until it reaches a maximum. At temperatures between 600 to 800 ^oC, the sewage sludge-derived syngas does not affect the NO concentration. At higher temperatures, the reburning efficiency of the analysed reburning fuel increases. The strongest NO reduction occurs at temperatures higher than 1000 ^oC; however, the best temperature for the reburning process is 1200 ^oC. In general, as seen in Fig. 4, increasing the molar ratio of reburning fuel results in a decrease in the temperature for optimal NO reduction.

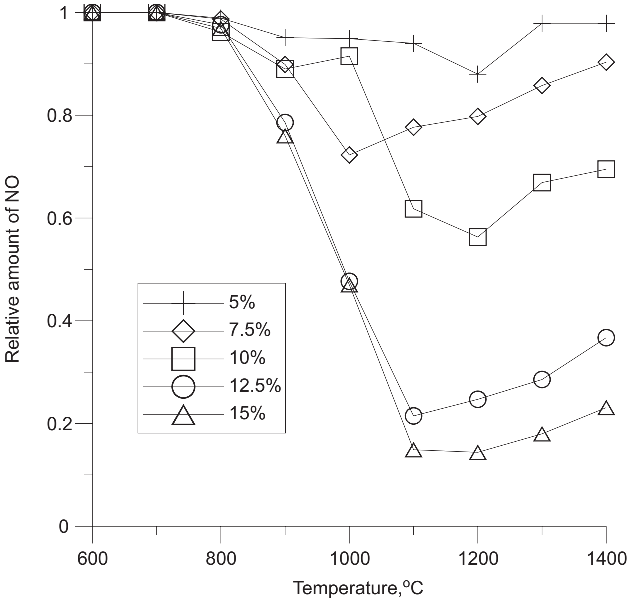

Fig. 4. Relative amount of NO_x as a function of the temperature for different values of the molar ratio of reburning fuel; λ – 1.1; τ = 0.4 s

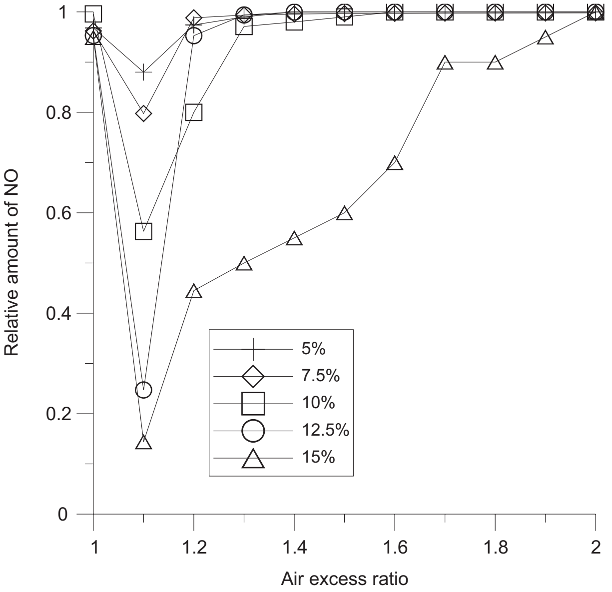

Fig. 5. Relative amount of NO_x as a function of the air excess ratio for different values of the molar ratio of reburning fuel; t = 1200 °C; τ = 0.4 s

Fig. 5 shows the dependence of relative amount of NO as a function of the air excess ratio for a reburning zone temperature and residence time of 1200 ^{o}C and 0.4 s. As shown in this figure, an air excess ratio equal to 1.0, reburning fuel has no influence on the reduction of NO. The reduction of NO increases up to a maximum as the stoichiometry becomes more fuel-rich. Such conditions favour the formation of CO and CO_2 via the oxidation mechanism of the reburning fuel instead of the formation of hydrocarbon radicals active in NO reduction. For each molar ratio of reburning fuel, the relative amount of NO initially decreases at the beginning as the air excess ratio begins to increase. As seen in this figure, there is a value of the air excess ratio for which the efficiency of the NO reduction reaches a maximum. Above this value, NO reduction decreases.

Conclusions

Alternative methods for the thermal utilization of sewage sludge are an important element in the wider problem of sludge disposal. Their undoubted advantage, in addition to the disposal of sludge, is that it becomes possible to obtain a product that can be effectively used for the generation of energy. Polish conditions also appear to present a good opportunity to utilize this group of waste-disposal technologies.

Acknowledgement

The paper has been prepared within the frame of the statute research of the Institute of Thermal Technology, Silesian University of Technology.

References

[1] The National Waste Management Plan 2014, Project. Warsaw: 2010.
[2] The National Urban Wastewater Treatment Program, Regulation of the Ministry of Environment. Warsaw: 2003.
[3] Werle S, Wilk RK. Renew Energy. 2010;35:1914-1919. DOI: 10.1016/j.renene.2010.01.019
[4] Regulation of the Minister of Economy and Labor on the admission criteria and procedures for the storage of waste in the landfill of the type of waste – Dz. U. 28 IX 2005r, 7 IX 2005.
[5] Werle S. Gaz, Woda i Technika Sanitarna. 2011;2:58-62.
[6] Kruczek S. Kotły. Wrocław: Oficyna Wydawnicza Politechniki Wrocławskiej; 2001.
[7] Buczynski R, Szlęk A. Chem Process Eng. 2007;28:189-197.
[8] Kim J-W, Mun T-Y, Kim J-O, Kim J-S. Fuel. 2011;90:2266-2272

ANALIZA MOŻLIWOŚCI ENERGETYCZNEGO WYKORZYSTANIA OSADÓW ŚCIEKOWYCH

Instytut Techniki Cieplnej
Politechnika Śląska w Gliwicach

Abstrakt: Promowanie wykorzystania odnawialnych źródeł energii jest jednym z priorytetów polskiej polityki energetycznej do roku 2030. Uważa się, iż współspalanie osadów ściekowych w warunkach polskich zasługują na szczególną uwagę. W pracy zaprezentowano dwa główne nurty badawcze. Pierwszy z nich dotyczy analizy możliwości współspalania komunalnych osadów ściekowych z węglem kamiennym w obiektach energetyki zawodowej. Drugi nurt dotyczy symulacji numerycznych procesu współspalania gazu ze zgazowania osadów ściekowych w kotle opalanym węglem kamiennym. Wnioski wskazują, iż energetyczne sposoby wykorzystania osadów ściekowych dają duże szanse na zastosowanie w polskich warunkach.

Słowa kluczowe: bezpośrednie współspalanie, pośrednie współspalanie, osady ściekowe

DOI: 10.2428/ecea.2012.19(01)016 ECOL CHEM ENG A. 2012;19(1-2):145-153

Katarzyna STEPANOWSKA, Marcin BIERNACZYK,
Artur OPANOWSKI and Zbigniew NEJA[1]

SELECTED MORPHOMETRIC CHARACTERS, CONDITION, AND BODY CHEMICAL COMPOSITION OF PERCH (*Perca fluviatilis* L.) FROM LAKE MIEDWIE, POLAND

WYBRANE CECHY MORFOMETRYCZNE, KONDYCJA ORAZ SKŁAD CHEMICZNY CIAŁA OKONI (*Perca fluviatilis* L.) Z JEZIORA MIEDWIE, POLSKA

Abstract: The study material comprised perch obtained from commercial catches conducted in May and November 2009 in Lake Miedwie. Catches were made using gill nets with a mesh size ranging from 40 to 45 mm. Fifty perch (25 from each of the catches) were obtained for the study. The fish were weighed [g], and then total length [mm] and maximum body height [mm] were measured. The dependencies between total length and weight, total length and body height, and weight and body height were calculated. The condition of the perch was determined with *Fulton's condition coefficient* (KF).

Twelve fish were chosen at random from among the study material collected in spring and autumn to determine body chemical composition. The mean weight of these individuals was 220.51 ± 18.68 g and mean length was 264.33 ± 6.86 mm in spring and 91.08 ± 17.20 g and 189.17 ± 7.52 mm in autumn, respectively. The stomachs were excised from the fish and their contents were identified. Gutted and deheaded fish were homogenized, and the percentage share of the following were determined according to Polish norms: protein, lipids, dry matter, and ash. Qualitative analysis of the fatty acid content of the fish was performed with the PN-EN ISO 5509: 2001 chromotagraphic method.

The results of the analyses indicate that the perch caught in May 2009 have greater body weights, lengths, and heights and higher quantities of lipid in comparison with the perch caught in autumn of 2009. The values of these parameters for spring and autumn, respectively, are as follows: body weight – 156.86 ± 15.98 and 86.46 ± 8.98 g; total length – 233.68 ± 7.37 and 189.08 ± 4.49 mm; body height – 52.66 ± 1.97 and 44.39 ± 1.59 mm; body lipid content – 1.32 ± 0.03 and 0.24 ± 0.01 %. However, the fish caught in November 2009 had higher KF, and contained more EPA and DHA fatty acids in comparison with fish caught in spring 2009, as follows (for spring and autumn, respectively): KF – 1.128 ± 0.02 and 1.203 ± 0.02; EPA content – 7.025 ± 0.005 and 8.725 ± 0.015 %; DHA content – 16.890 ± 0.030 and 18.575 ± 0.005 %.

Keywords: perch, condition, protein, lipids, fatty acids, Miedwie lake

---

[1] Department of Marine Biological Resources, Faculty of Food Sciences and Fisheries, West Pomeranian University of Technology in Szczecin, ul. Kazimierza Królewicza 4, 70-110 Szczecin, Poland, phone: +48 91 449 66 82, email: greyseal@o2.pl

Lake Miedwie is a deep, post-glacial trough basin with a surface area of 3527 ha, and it is the largest freshwater lake in West Pomerania. Since it is a water source for the city of Szczecin, Lake Medwie and its tributaries are monitored annually. Based on the prevailing hydrochemical conditions, this lake is classified as mesotrophic [1, 2].

Intense fisheries have been conducted in Lake Medwie for many years, and, currently, catches of perch, *Perca fluviatilis* L. (*Perciformes*), are significant source of fishermen income in this basin (Fig. 1). Although perch is a lean fish, consumer demand for its meat is high because of its excellent taste, its easily assimilable protein, and its high content of fatty acids from the n-3 and n-6 families [3-6].

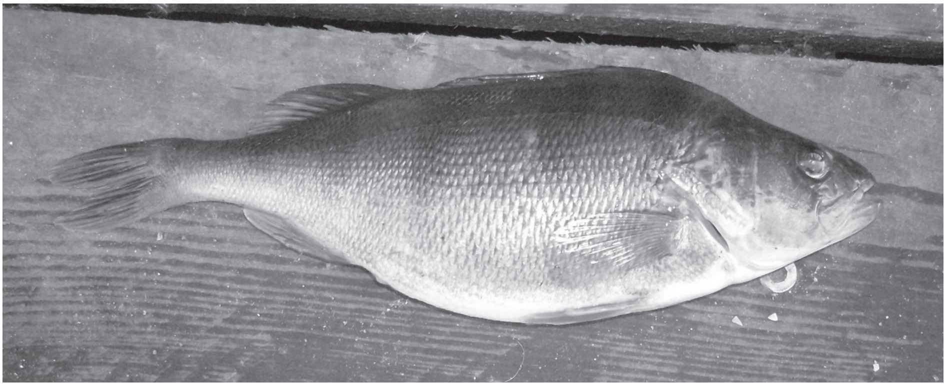

Fig. 1. Perch (*Perca fluviatilis* L.)

Since the occurrence of perch dominates the catches made in Lake Miedwie, it was decided to determine the dependencies in this species between length and weight, the condition coefficient, and the chemical composition of their bodies with a particular focus on the fatty acids.

Materials and methods

The study material comprised perch obtained from commercial catches conducted in spring (05.2009) and autumn (11.2009) in Lake Miedwie. Catches were made using gill nets with a mesh size ranging from 40 to 45 mm. Fifty perch (25 from each of the catches) were obtained for the study. The fish were weighed [g], and then total length [mm] and maximum body height [mm] were measured. The dependencies between total length and weight, total length and body height, and weight and body height were calculated. The condition of the perch was determined with *Fulton's coefficient* (KF) using the following formula:

$$KF = \frac{W \times 100000}{TL^3}$$

W – *total weigh*t of fish [g];
TL – *total length* of fish [mm].

Twelve fish of mean weight 220.51 ± 18.68 g and mean length 264.33 ± 6.86 mm in spring and another twelve fish of mean weight 91.08 ± 17.20 g and mean length 189.17 ± 7.52 mm in autumn were chosen at random from among the samples taken from the spring and autumn catches to determine the chemical composition of their bodies. The stomachs were excised and the contents identified. The gutted and deheaded fish were homogenized and the percentage shares of the following were determined according to the Polish norms:

– total protein – Kjeldahl method;
– raw lipids – Soxhlet method;
– dry matter – samples were dried at a temperature of 105 ^{o}C for 12 h;
– ash – samples were pyrolized at a temperature of 550 ^{o}C for 10 h.

The fatty acid contents of the fish were analyzed qualitatively with the PN-EN ISO 5509: 2001 chromatographic method.

The results were analyzed statistically with STATISTICA 7.1 operating in a Windows environment [7], and the graphs were generated with Microsoft Office Excel 2003.

Results

The perch caught in May 2009 weighed more, had longer total lengths, and higher maximum body heights in comparison with the fish caught in November 2009 (Table 1).

Table 1

Mean weight [g], total length [mm] and body height [mm] of perch caught in May and November 2009, x ± SEM, n = 50

	May 2009	November 2009
Weight [g]	156.86 ± 15.98	86.46 ± 8.98**
TL [mm]	233.68 ± 7.37	189.08 ± 4.49**
Height [mm]	52.66 ± 1.97	44.39 ± 1.59**

** Statistically different differences at $p \le 0.01$.

The dependence of body length on weight in the fish caught in spring took the form of the exponential equation $y = 5.5016e^{0,0138x}$; in autumn, the exponential equation was $y = 3.3278e^{0.0168x}$ (Fig. 2). The dependence of body height and weight in fish caught in spring took the form of the exponential equation $y = 9.1778e^{0.0515x}$, while in autumn it was $y = 10.4770e^{0.0457x}$ (Fig. 3). The value for the dependence of length and body height of the fish caught in spring took the form of the linear equation $y = 0.2578x – 7,5869$, while in autumn it was $y = 0.3286x – 17.7480$ (Fig. 4).

The value of Fulton's condition coefficient was statistically ($p \le 0.01$) higher in the perch caught in November in comparison to the fish caught in May 2009 (Table 2).

Significant changes were noted in the chemical composition of fish body from the catches made in May and those from the November 2009 catches (Table 3).

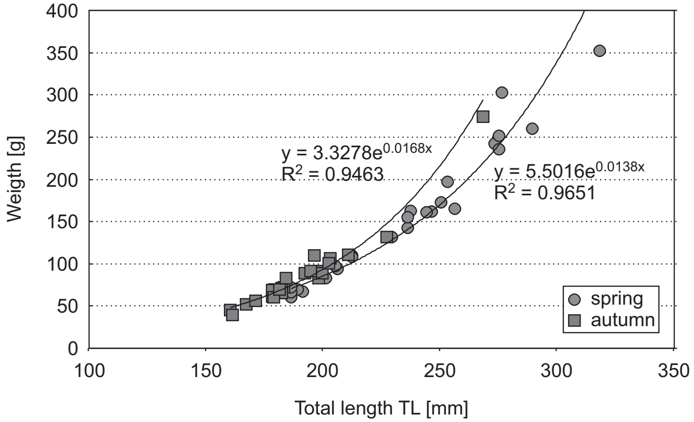

Fig. 2. Length-weight dependency

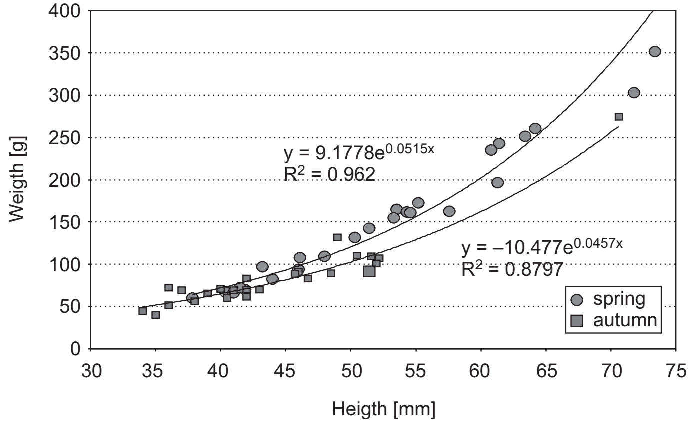

Fig. 3. Height-weight dependency

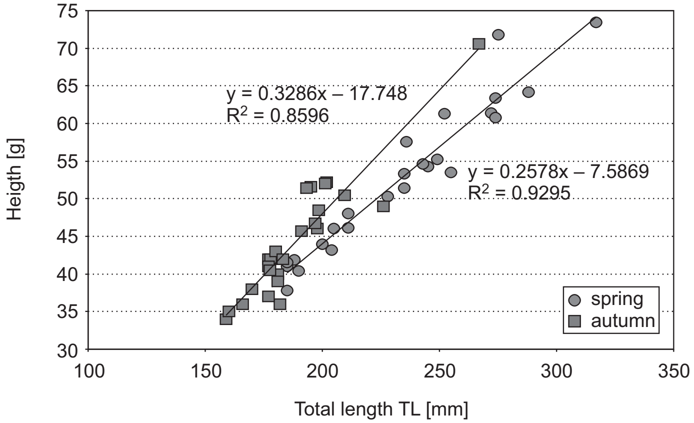

Fig. 4. Length-height dependency

Table 2

Fulton's condition coefficient (KF) of perch caught in May and November 2009, x ± SEM, n = 50

May 2009	November 2009
1.128 ± 0.02	1. 203 ± 0.02*

* Statistically significant differences at $p \leq 0.05$.

Table 3

Proximal composition of perch caught in May and November 2009 [%] x ± SEM

Chemical component	May 2009	November 2009
Dry matter	21.14 ± 0.07	19.42 ± 0.06**
Total protein	19.35 ± 0.07	19.39 ± 0.04
Lipids	1.32 ± 0.03	0.24 ± 0.01**
Ash	1.46 ± 0.01	1.25 ± 0.03*

** Statistically different differences at $p \leq 0.01$; * statistically significant differences at $p \leq 0.05$.

Qualitative analyses of the lipid composition indicated there were significant differences in the levels of selected fatty acids from the n-3 and n-6 families between the fish from catches made in May and November 2009 (Table 4).

Table 4

Composition of fatty acids [%] of perch caught in May and November, x ± SEM, n = 50

Acid		May 2009	November 2009
Miristic	C 14:0	2.970 ± 0.010	1.030 ± 0.030**
Miristicoleic	C 14:1	0.365 ± 0.015	0.050 ± 0.000**
Palmitic	C 16:0	13.155 ± 0.015	20.495 ± 0.095**
Palmitoleic	C 16:1	9.115 ± 0.015	4.405 ± 0.035**
Stearic	C 18:0	2.255 ± 0.015	4.440 ± 0.050**
Oleic	C 18:1	17.795 ± 0.135	11.965 ± 0.015**
Linoleic	C 18:2	3.880 ± 0.030	3.395 ± 0.015**
Gamma linolenic	C 18:3n6	0.030 ± 0.010	< 0.01
Alfa linolenic	C 18:3n3	4.955 ± 0.025	1.990 ± 0.030**
Arachidic	C 20:0	0.090 ± 0.000	< 0.01
Eicosenoic	C 20:1	0.340 ± 0.020	0.365 ± 0.005**
Eicosadienoic	C 20:2	0.240 ± 0.000	0.300 ± 0.000
Eicosatrienoic	C 20:3	0.335 ± 0.015	0.190 ± 0.000*
Arachidonic	C 20:4	3.790 ± 0.000	8.845 ± 0.005**
Eicosapentaenoic (EPA)	C 20:5	7.025 ± 0.005	8.725 ± 0.015**
Erucic	C 22:1	< 0.01	< 0.01
Docosapentaenoic	C 22:5	1.310 ± 0.000	< 0.01
Docosahexaenoic (DHA)	C 22:6	16.890 ± 0.030	18.575 ± 0.005**
Nervonic	C 24:1	0.130 ± 0.000	< 0.01

** Statistically different differences at $p \leq 0.01$; * statistically significant differences at $p \leq 0.05$.

Discussion

Perch catches are an important source of income for the commercial fishers operating in Lake Miedwie. In the current study, the body measurements of the fish caught in spring were greater than those of fish caught in autumn. However, the fish caught in the autumn had a higher Fulton's condition coefficient in comparison with that of the perch caught in May 2009. The condition of the perch examined in this study was comparable to that of the same species from the Solina (1.23–1.55) and Roznow (1.27–1.62) dam reservoirs [8]. It was, however, lower than the values of the condition coefficient (2.13) noted by Szypula [9] for perch from Lake Miedwie in the 1997–2000 period. It must be emphasized that Szypula [9] determined the condition coefficient of the fish using *standard length* (SL) in the equation and not *total length* (TL) as was done in the present study. The occurrence of larger individuals in the spring catches than in those made in the autumn could be linked to the season of the year and perch spawning. The measurements taken for the current study provide the basis for concluding that the length, weight, and height of the perch examined during the current study in different seasons of the year were strongly mutually correlated.

The analysis of perch food indicated that they fed primarily on small fish (mainly bleak). Most of the stomachs examined were empty, which is likely a consequence of storms that occurred prior to the catches in both the spring and autumn.

Fish are divided into three groups according to the lipid content of their muscles: fatty fish contain more than 5 % fat; moderately fatty fish contain from 1–5 % fat; lean fish contain up to 1 % fat [10]. According to the table of nutritional norms by Kunachowicz [11], the fat content of perch is 0.8 %, which places this fish in the lean category. This might indicate that the main nutritional value of perch meat for the consumer is its easily assimilable protein, the content of which remains at high levels regardless of the season of the year. The analysis of the proximate composition of the perch examined indicated that the lipid content in perch from Lake Miedwie during the spring is relatively high which permits classifying these fish as moderately fatty during this period.

Stanek et al [5] observed a different phenomenon in their study of perch females from the Wloclawski Reservoir; the lipid content in these fish was 1.97 ± 0.58 % in June and 2.17 ± 0.54 % in December. In their study of the annual chemical composition of perch body from the River Mouse, Blanchard et al [3] observed lower lipid levels in perch tissues in June (0.564 %) than in October (0.633 %). Neja et al [12] also studied perch from Lake Miedwie in the autumn period and noted relatively high lipid levels (1.71 ± 0.04 %). Presumably, the low lipid levels noted in the perch in the autumn during the current study were the result of a long storm that disrupted normal feeding prior to the catches.

While the content of easily assimilable protein and lipids is important, the nutritional value of fish meat is determined largely by the content of polyunsaturated fatty acids from the *n*-6 and *n*-3 families. *Eicosapentaenoic* (EPA) and *docosahexaenoic* (DHA) acids, which are long-chain fatty acids of the *n*-3 family, play important roles in the human body. In addition to their significance in preventing and treating lifestyle diseases, these acids are also key to a variety of physiological functions [13; 14]. EPA is an important stimulator of the cardiac and circulatory systems, while DHA is a component of nerve tissues, the brain stem, and the eyes, which means that it can have a significant impact on vision [15]. DHA is essential to the workings of the brain, has an impact on intelligence, and can also aid in relieving the symptoms of stress [16].

Many studies indicate that the type and content of fatty acids in fish depend on the species, their physiological state, the basin they inhabit, the season of the year, hydrochemical conditions, and feeding behavior [17–21].

The lipids of fish from cold northern seas have higher levels of eicosapentaenoic (EPA) fatty acids, while fish from southern seas contain more docosahexaenoic (DHA) fatty acids [13]. It has been demonstrated recently that in addition to marine fish, freshwater fish can be a good source of polyunsaturated fatty acids [16, 22–24]. Bieniarz and Koldras [25] reported that the European wels, pike, and rainbow trout all have lipids that are similar to those of marine fish species in both quantity and composition.

In the current study, significantly higher percentage shares of EPA and DHA were noted in perch in autumn in comparison with spring, which could have resulted from the impact of water temperature, feeding behavior, and the spring spawning period. Similar tendencies were observed in female perch from the Wloclawski Reservoir, and it is notable that the percentage content of EPA was similar while that of DHA was significantly lower than the levels recorded in perch from Lake Miedwie [5]. Similar levels of the fatty acids EPA and DHA were noted in perch from the River Mouse. However, despite a significant increase in the content DHA fatty acid in the fish from this river from June to October, there was a decrease in the content of fatty acid EPA [3].

To summarize, it was concluded that perch from spring and autumn catches differ in body size, condition, and body chemical composition. The fish caught in May 2009 were characterized by greater weight, length, and body height as well as a higher body fat content. Perch caught in November, however, had higher values of the condition coefficient (KF) and higher contents of EPA and DHA fatty acids. These difference were undoubtedly linked to the season of the year, feeding behavior, and the physiological state of the perch examined.

References

[1] Machula S, Tórz A. Ocena jakości wód Jeziora Miedwie w okresie jesienno-wiosennym 1999-2000. V międzynarodowa konferencja naukowo-techniczna “Zaopatrzenie w wodę i jakość wód” Poznań-Gdańsk, Polska: 2002;221-231.

[2] Tórz A, Kubiak J, Chojnacki JC. Assessment of Lake Miedwie water quality in 1998-2001. Acta Sci Polon. 2003;2(1):279-290.

[3] Blanchard G, Druart X, Kestemont P. Lipid content and fatty acid composition of target tissues in wild Perca fluviatilis females in relation to hepatic status and gonad maturation. J Fish Biol. 2005;66:73–85.

[4] Orban E, Nevigato T, Masci M, di Lena G, Casini I, Caproni R, Gambell L, de Angelis P, Rampaccii M. Nutritional quality and safety of European perch (Perca fluviatilis) from three lakes of Central Italy. Food Chem. 2007;100:482-490.

[5] Stanek M, Dąbrowski J, Roślewska A, Kupcewicz B, Janicki B. Impact of different fishing seasons on the fatty acids profile, cholesterol content, and fat in the muscles of perch, Perca fluviatilis L. from the Włocławski Reservoir (central Poland). Arch.Polon Fish. 2008;16(2):213-220.

[6] Xu XL, Fontaine P, Melard C, Kestemont P. Effects of dietary fat levels on growth, feed efficiency and biochemical compositions of Eurasian perch Perca fluviatilis. Aquac Int. 2001;9:437-449.
[7] StatSoft, Inc. 1984-2005, STATISTICA for Windows [Computer program manual]. Tulsa, OK: StatSoft, Inc., 2325 East 13th Street, Tulsa, OK, 74104, (918) 583–4149, fax: (918) 583-4376, e-mail: info@statsoft.com, WEB: http://www.statsoft.com
[8] Epler P, Łuszczek-Trojnar E, Socha M, Drąg-Kozak E, Szczerbik P. Age and growth of the perch (Perca fluviatilis L.) in the Solina and Roznow dam reservoirs. Acta Sci Polon. 2005;4(1-2):43-50.
[9] Szypuła J. The length-weight relationship and condition of pike and perch in lake Miedwie. Acta Ichthyol Piscat. 2002;32(1):93-106.
[10] Sikorski ZE. Technologia żywności pochodzenia morskiego, Warszawa: WNT; 1980.
[11] Kunachowicz H, Nadolna I, Przygoda B, Iwanow K. Tabele wartości odżywczej produktów. Warszawa: Instytut Żywności i Żywienia; 1998.
[12] Neja Z, Biernaczyk M, Opanowski A, Czerniejewski P, Stepanowska K. Selected morphometric characteristics and body chemical composition of perch (Perca fluviatilis L.). X Meždunarodnoj naučno-praktičeskoj konferencii molodyh učënyh, studentov i aspirantov: Analiz i prognozirovanie sistem upravleniâ: Trudy: Čast' I Sankt-Peterburg: Izdatel'stvo SZTU, 2009;308-314.
[13] Budzyńska-Topolowska J, Ziemlański Ś. Rola wielonienasyconych kwasów tłuszczowych z rodziny n-3 w zapobieganiu i leczeniu miażdżycy. Czynniki Ryzyka. 1993;2:55-63.
[14] Ziemlański Ś, Budzyńska-Topolowska J. Współczesne poglądy na rolę fizjologiczną wielonienasyconych kwasów tłuszczowych z rodziny n-3. Żyw. Człow. Metab. 1992;1:41-47.
[15] Connor WE, Neuringer M, Reisbick S. Essential fatty acids: The importance of n-3 fatty acids in the retina and brain. Nutr Rev. 1992;50(4):21-29.
[16] Arts M, Ackman RG, Holub BJ. "Essential fatty acids" in aquatic ecosystems:a crucial link between diet and human health and evolution. Can Fish Aqua. Sci. 2001;58:122-137.
[17] Geurden I, Coutteau P, Sorgeloos P. Increased docosahexaenoic acid levels in total and polar lipid of European sea bass (Dicentrarchus labrax) postlarvae fed vegetable or animal phospholipids. Mar Biol. 1997;129:689-698.
[18] Kołakowska A, Szczygielski M, Bienkiewicz G, Zienkowicz L. Some of fish species as a source of n-3 polyunsaturated fatty acids. Acta Ichthyol Piscat. 2000;30(2):59-70.
[19] Kamler E, Krasicka B, Rakusa-Suszczewski S. Comparision of lipid content and fatty acid composition in muscle and liver of notothenioid fishes from Admiralty Bay (Antarctica): an eco-physiological perspective. Pola. Biol. 2001;24:735-743.
[20] Rueda FM, Hernández MD, Egea MA, Aguado F, García B, Martínez F.J. Differences in tissue acid composition between reared and wild sharpsnout sea bream, Diplodus puntazzo (Cetti, 1777). Brit J Nutr. 2001;86:617-622.
[21] Dwyer KS, Parrish CC, Brown JA. Lipid composition of yellowtail flounder (Limanda ferruginea) in relation to dietary lipid intake. Mar Biol. 2003;143:659-667.
[22] Ahlgren G, Blomqvist P, Boberg M, Gustafsson JB. Fatty acids content of the dorsal muscle – an indicator of fat quality in freshwater fish. J Fish Biol. 1994;45:131-157.
[23] Steffens W. Effects of variation in essential fatty acids in fish feeds on nutrive value of freshwater fish for humans. Aquac. 1997;151:97-119.
[24] Bieniarz K, Kołdras M, Kamiński J, Mejza T. Fatty acids, fat and cholesterol in some lines of carp (Cyprinus carpio L.) in Poland. Arch Polish Fish. 2001;9(1):5-24.
[25] Bieniarz K, Kołdras M. Kwasy tłuszczowe i cholesterol w mięsie ryb. Kom Ryb. 2000;6:25-29.

WYBRANE CECHY MORFOMETRYCZNE, KONDYCJA ORAZ SKŁAD CHEMICZNY CIAŁA OKONI (*Perca fluviatilis* L.) Z JEZIORA MIEDWIE, POLSKA

Wydział Nauk o Żywności i Rybactwa
Zachodniopomorski Uniwersytet Technologiczny w Szczecinie

Abstrakt: Materiał do badań stanowiły okonie pochodzące z połowów gospodarczych prowadzonych wiosną (05.2009) oraz jesienią (11.2009) w jeziorze Miedwie. Połowy ryb prowadzone były wontonami o rozmiarach oczka od 40 do 45 mm. Do badań pozyskano 50 okoni, po 25 sztuk z każdego połowu. Ryby ważono [g], a następnie mierzono ich długość całkowitą l.t. [mm] oraz maksymalną wysokość ciała [mm]. Ponadto obliczono relację długości całkowitej do masy badanych ryb. Obliczono także relację długości całkowitej do wysokości badanych ryb oraz masy badanych ryb do ich wysokości. Kondycję okoni określano za pomocą *współczynnika kondycji Fultona* (KF).

Ponadto spośród złowionych ryb, zarówno wiosną jak i jesienią, wybrano losowo po 12 sztuk o średniej masie 218 ± 74 g i długość l.t. 218 ± 74 mm w celu oznaczenia składu chemicznego ich ciała. Od ryb pobrano żołądki i oznaczono ich zawartość. Wypatroszone i odgłowione ryby zhomogenizowano i w tak uzyskanej próbie oznaczono wg Polskiej Normy procentową zawartość białka, tłuszczu, suchej masy i popiołu. Przeprowadzona została także analiza jakościowa tłuszczu zawartego w ciele ryb metodą chromatografii PN-EN ISO 5509: 2001.

Na podstawie przeprowadzonych badań można stwierdzić, że okonie odłowione w maju charakteryzowały się większą masą, długością oraz wysokością ciała, a także większą zawartością tłuszczu w ciele w porównaniu do ryb odłowionych jesienią 2009 r.; odpowiednio wiosną i jesienią: masa ciała – 156,86 ± 15,98 i 86,46 ± 8,98 g; długość całkowita – 233,68 ± 7,37 i 189,08 ± 4,49 mm; wysokość ciała – 52,66 ± 1,97 i 44,39 ± 1,59 mm; ilość tłuszczu w ciele – 1,32 ± 0,03 i 0,24 ± 0,01%. Natomiast okonie odłowione w listopadzie charakteryzowały się większą wartością *współczynnika kondycji* (KF) oraz większą zawartością kwasów tłuszczowych EPA i DHA w ciele w porównaniu do ryb odłowionych wiosną 2009 r.; odpowiednio wiosną i jesienią: współczynnik kondycji (KF) – 1,128 ± 0,02 i 1,203 ± 0,02; zawartość EPA – 7,025 ± 0,005 i 8,725 ± 0,015 %; zawartość DHA – 16,890 ± 0,030 i 18,575 ± 0,005 %.

Słowa kluczowe: okoń, kondycja, białka, tłuszcz, kwasy tłuszczowe, jezioro Miedwie

DOI: 10.2428/ecea.2012.19(01)017 ECOL CHEM ENG A. 2012;19(1-2):155-159

Barbara SKWARYŁO-BEDNARZ[1]

INFLUENCE OF CONTAMINATION OF SOIL WITH COPPER ON THE ACTIVITY OF DEHYDROGENASES IN AREAS WHERE AMARANTHUS IS CULTIVATED

WPŁYW ZANIECZYSZCZENIA GLEBY MIEDZIĄ NA AKTYWNOŚĆ DEHYDROGENAZ POD UPRAWĄ AMARANTUSA

Abstract: The pot experiment investigated the influence of various dosages of copper (0, 20, 40, 80, 120 mg · kg^{-1} of soil) on the activity of dehydrogenases in the soils in which amaranthus, Rawa variation, was cultivated. The pot experiment revealed that the highest activity of dehydrogenases could be observed when no fertilization with Cu was applied, and the lowest activity of dehydrogenases occurred with the highest dosage of Cu in the experimental pot. An increase in the activity of dehydrogenases was found in the control objects and objects where the lowest dosage of copper was applied in the investigated period (June–August––October). Addition of increased dosages of copper resulted in the decrease of the activity of dehydrogenases in the investigated months, as related to the control objects. Significant high negative correlations was found between the dosage of Cu that was applied and activity of dehydrogenases in the investigated months.

Keywords: amaranthus, activity of dehydrogenases, copper

Amaranthus is a universal plant [1], and is grown mainly to obtain seeds that are rich in nutrients. It can also be used for energy purposes. A growing interest in cultivating Amaranthus in Poland, especially the south-eastern part of the country, encourages studies that can estimate the influence of this plant on enzymatic activity of soil environment. Initial studies suggest that amaranthus has a stimulating effect in development of soil microflora and enzymatic activity [2]. Such a beneficial influence of amaranthus on biological properties of soil environment can be used in studies, and then in attempts to improve the activity of soils that have been degraded by excessive accumulation of heavy metals, namely: copper. It should be noted that contamination of soil with copper leads to bioaccumulation of this element, and affects plant – soil homeostase, which can lead to degradation of soil environment [3].

---

[1] Faculty of Agricultural Sciences in Zamosc, University of Life Sciences in Lublin, ul. Szczebrzeska 102, 22–400 Zamość, Poland, phone: +48 84 677 27 56, email barbara.skwarylo@up.lublin.pl

The aim of the study was to evaluate the influence of contamination of soil with growing dosages of copper on the activity of dehydrogenases in soil environment in areas where amaranthus, Rawa variety, is cultivated.

Material and methods

The experiment was carried out in plastic pots which capacity was 3.5 kg in three replications. The pots were filled with silt loam (pH 6.6) marked in solution of KCl with concentration 1 mol $\cdot$ dm^{-3}. Before amaranthus, Rawa variation, was sown, uniform fertilization with macroelements was applied in the following dosages counted for pure element [g $\cdot$ kg^{-1} of soil]: N – 0.25, P – 0.10, K – 0.10.

Variable factors in the experiment were dosages of copper [mg $\cdot$ kg^{-1} of soil]: 0; 20; 40; 80; 120; (in the form of $CuSO_4 \cdot 5H_2O$). The seeds were sown on 26.05.2008. After sprouting 3 plants were left in each pot. The experiment spread over the whole vegetation period of amaranthus. 5 soil samples were taken (into plastic bags) from each pot in order to obtain the mean sample. The soil was carefully mixed, and then sifted through a sieve with 2 mm holes. Soil was taken from each mean sample for analysis of the activity of dehydrogenases. Activity of dehydrogenases was determined in June, August, and October. The study included marking the activity of dehydrogenases with Thalmann's method [4]. 5 g portions of soil were put into 100 cm^3 flasks, and then 5 cm^3 of 1 % Triphenyltetrazolium chloride (TCC) was added which had earlier been dissolved in Tris-HCl buffer with pH 7.4. The soil samples were incubated for 96 hours at temperature of 30 ^{o}C, then 20 cm^3 of methanol was added to each flask. Next, the samples were shaken out for five minutes and filtered. The filtrate was marked spectrophotometrically at wavelength λ = 485 nm.

Results and discussion

Enzymatic activity of soils is considered to be a sensitive indicator of both favourable and unfavourable changes that take place in soil environment [5, 6]. Evaluation of dehydrogenase activity in soil is of particular importance. In many papers, the activity of dehydrogenases in soil is often referred to as total microbiological activity of soil environment [7].

Moreover, enzymatic activity of soil, and especially the activity of dehydrogenases, can be considered as an indicator of contamination with heavy metals [8]. Excess of heavy metals, such as copper, is harmful because they contaminate soils and decrease biochemical activity of soil, and are also harmful for plants, animals, and humans [9]. Cultivation of plants that are used as food in soils with higher contents of heavy metals or contaminated soils is not advisable. However, energy plants are often cultivated in such soils. Planting amaranthus in areas that are contaminated with heavy metals can decrease contamination with heavy metals.

The investigation that was carried out reveals, that the highest values of dehydrogenase activity in the analysed months (June, August, October) were found in control objects, where no copper was applied (Table 1). It was observed that the value of dehydrogenase activity in the consecutive months of the analysis decreased alongside with the increase in the contents of copper in soil (Table 1).

Table 1

Activity of dehydrogenases in the investigated months depending on contamination of soil with copper (mean values)

Cu dose [mg · kg^{-1} of soil]	Dehydrogenases activity [mg TPF · kg^{-1} · day^{-1}]		
	June	August	October
0 (control object)	9.5	17.8	25.5
20	9.4	17.4	24.5
40	8.8	14.0	9.0
80	7.0	12.2	6.8
120	4.4	6.2	6.5

Throughout the experiment, it was determined, that the activity of dehydrogenases gradually increased only in soil from control objects and soil in which the lowest docsage of Cu had been applied. Application of higher dosages of Cu (40 mg · kg^{-1}, 80 mg · kg^{-1}, and 120 mg · kg^{-1}) increased the activity of dehydrogenases in June–August, and then it decreased from August to October (Table 1).

The activity of dehydrogenases in June in the control objects was 9.5 mg TPF · kg^{-1} · day^{-1}. When 20 mg · kg^{-1} of Cu was applied, the activity of dehydrogenases was only 1.1 % lower than in the control objects. Application of dosages of Cu into the soil (40 mg · kg^{-1} Cu, 80 mg · kg^{-1} Cu, and 120 mg · kg^{-1} Cu), caused a decrease of the activity of dehydrogenases by 7.4 %, 26.3 % and 53.7 %, respectively (Table 1).

The activity of dehydrogenases in August in the control objects was 17.8 mg TPF · kg^{-1} · day^{-1}. It was 2.2 % higher when compared with the first dosage that had been applied, and 21.3 %, 31.5 % and 65.2 % higher for the consecutive, increased dosages (Table 1).

The activity of dehydrogenases in October in the control objects was 25.5 mg TPF · kg^{-1} · day^{-1}, and it was the highest value that was recorded. A slightly lower activity of dehydrogenases was observed in the objects where the lowest dosage of Cu had been applied – 24.5 mg TPF · kg^{-1} · day^{-1}, which was by 3.9 % lower than in the control objects. Significantly lower activity of dehydrogenases was observed in the objects where 40 mg · kg^{-1} Cu had been applied (64.7 % decrease), 80 mg · kg^{-1} Cu (73.3 % decrease), and 120 mg · kg^{-1} Cu (74.5 % decrease), as compared with the control objects (Table 1).

The investigation clearly reveals that application of copper into the soil, especially in the highest dosage used in the experiment, causes a decrease in the activity of dehydrogenases in the soil. Similar correlations were observed by Nowak et al [10]. The authors claimed, that when contamination of soil with heavy metals increased, the activity of dehydrogenases significantly decreased. Negative effects of copper in the activity of dehydrogenases were also observed by Kucharski and Hlasko-Nasalska [11].

The statistical analysis that was carried out also revealed significant negative correlation between the dosage of copper that had been applied and the activity of dehydrogenases in the soil where amaranthus was cultivated (Table 2).

Table 2

Correlation coefficients between the dosages of Cu that had been applied [mg · kg^{-1} of soil] and the activity of dehydrogenases in the soil where amaranthus was cultivated, at $p = 0.01$

Cu dose [mg · kg^{-1} of soil]	Dehydrogenases activity [mg TPF · kg^{-1} · day^{-1}]		
	June	August	October
	–0.974	–0.976	–0.850

Conclusions

1. The highest activity of dehydrogenases in the pot experiment was found in the object where no Cu fertilisation had been used.
2. A successive increase in the activity of dehydrogenases was observed in the control objects, and the objects where the lowest dosage of Cu had been applied in the experimental period (June–August–October).
3. Application of higher dosages of copper (40, 80, 120 mg · kg^{-1}) caused a decrease in the activity of dehydrogenases in the investigated months, as compared with the control objects. It was observed, that the objects where dosages of Cu had been applied showed an increase in the activity of dehydrogenases in June–August, and a decrease in this activity in August–October.
4. Significant negative correlation between the dosage of copper that had been applied and the activity of dehydrogenases in the soil were observed in the investigated months.

References

[1] Nalborczyk E. Rolnicza energetyka. Biomasa jako źródło ekologicznej energii. Academia. 2005;3(7):16-19.

[2] Skwaryło-Bednarz B. Ocena właściwości biologicznych gleby pod uprawą szarłatu (*Amaranthus cruentus* L.). Acta Agrophys. 2008;12(2):527-534.

[3] Karoń B, Gediga K. Wpływ wysokich dawek miedzi i wapnowania na plonowanie i skład chemiczny owsa. Zesz Nauk Pol Akad Nauk Kom Nauk Prezyd PAN Człow Śr. 1996;14:134-138.

[4] Gostkowska K, Furczak J, Domżał H, Bielińska J. Suitability of some biochemical and microbiological tests for the degradation degree of podzolic soil on the background of its differentiated usage. Pol J Soil Sci. 1998;31:69-78.

[5] Koper J, Siwik A. Wpływ emisji zanieczyszczeń na aktywność enzymatyczną gleby w rejonie Zakładów Azotowych we Włocławku. Zesz Prob Post Nauk Roln. 2000;472:413-420.

[6] Januszek K, Błońska E, Stanik P. Comments concerning determination of dehydrogenase activity in soil by the TTC-formazan test. Acta Agrophys.2007;9(3):635-644.

[7] Nadgórska-Socha A, Łukasik I, Ciepał R, Pomierzy S. Activity of selected enzymem in soil loaded with varied levels heavy metals. Acta Agrophys. 2006;8(3):713-725, 2006.

[8] Korzeniowska J, Stanisławska-Glubiak E. Phytotoxic concentration of some heavy metals in soils. Zesz Probl Post Nauk Rol. 2003;493:167-173.

[9] Rozporządzenie Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi, Dz. U. Nr 165, poz. 1359 (in Polish).
[10] Welp G. Inhibitory effects of the total and water-soluble concentrations of nine different metals on the dehydrogenase activity of a less soil. Bio Fert Soils. 1999;30:32-139.
[11] Thalmann A. Zur Methodik der Bestimmung der Dehydrogenaseactivität in Boden mittels Triphenyltetrazolium chlorid (TTC). Landwirtsch Forsch. 1968;21:249-258.
[12] Trawczyńska A. Próba oceny wpływu zakwaszenia gleby na jej aktywność biologiczną w aluwiach górnego odcinka doliny Bzury. Zesz Prob Post Nauk Roln. 1998;456:243-249.
[13] Wyszkowska J, Kucharski J. Liczebność drobnoustrojów w glebie zanieczyszczonej metalami ciężkimi. Zesz Prob Post Nauk Roln. 2003;492:427-433.
[14] Wyszkowska J, Kucharski J. Właściwości biochemiczne i fizykochemiczne gleby zanieczyszczonej metalami ciężkimi. Zesz Prob Post Nauk Roln. 2003;492:435-442.
[15] Nowak J, Niedźwiecki E, Dziel M. Wpływ metali ciężkich na zmiany aktywności enzymatycznej gleby. Rocz Glebozn. 1999;1(1/2):61-68.
[16] Kucharski J, Hłasko-Nasalska A. Crops yielding and soil enzymatic acticity as affected by copper contamination. Acta Agraria et Silvestria Series Agraria. 2005;XLV:55-63.

WPŁYW ZANIECZYSZCZENIA GLEBY MIEDZIĄ NA AKTYWNOŚĆ DEHYDROGENAZ POD UPRAWĄ AMARANTUSA

Wydział Nauk Rolniczych w Zamościu
Uniwersytet Przyrodniczy w Lublinie

Abstrakt: W doświadczeniu wazonowym oceniano wpływ różnych dawek miedzi (0, 20, 40, 80, 120 mg · kg^{-1} gleby) na aktywność dehydrogenaz w glebie pod uprawą szarłatu odmiany Rawa. W warunkach przeprowadzonego doświadczenia wazonowego najwyższą aktywnością dehydrogenaz charakteryzowały się obiekty bez zastosowanego nawożenia Cu, a najniższą obiekty z najwyższą dawką tego mikroelementu. Stwierdzono wzrost aktywności dehydrogenaz w obiektach kontrolnych oraz wraz z zaaplikowaną najmniejszą dawką miedzi w badanym okresie (czerwiec–sierpień–październik). Dodanie większych dawek miedzi przyczyniło się do zmniejszenia aktywności dehydrogenaz w badanych miesiącach w porównaniu z obiektami kontrolnymi. Stwierdzono, że obiekty z tymi dawkami wykazują wysokie istotne ujemne zależności pomiędzy zaaplikowaną dawka Cu a aktywnością dehydrogenaz w badanych miesiącach.

Słowa kluczowe: amaranthus, aktywność dehydrogenaz, miedź

DOI: 10.2428/ecea.2012.19(01)018 ECOL CHEM ENG A. 2012;19(1-2):161-168

Katarzyna GRATA[1]

EFFECT OF UREA PHOSPHATE ON THE *Bacillus* sp. POPULATION IN SOIL AND ANTIFUNGAL ACTIVITY OF SELECTED STRAINS ON *Fusarium* sp.

WPŁYW FOSFORANU MOCZNIKA NA LICZEBNOŚĆ BAKTERII Z RODZAJU *Bacillus* W GLEBIE I AKTYWNOŚĆ PRZECIWGRZYBOWĄ WYBRANYCH SZCZEPÓW NA *Fusarium* sp.

Abstract: The main objective of the examination was to assess the influence of urea phosphate (UP) on the number of *Bacillus* sp. and antifungal activity both *Bacillus subtilis* and *Bacillus amyloliquefaciens* on *Fusarium* sp. Fungal growth was evaluate on the basis of fungal spore germination and rate index of mycelium growth. Studies revealed positive influence of objects with urea phosphate on the number the *Bacillus* sp. The number of those microorganism was higher than in the non-manured and manured with FYM soil assayed throughout the experiment period. The spore germination of all *Fusarium* species were strongly inhibited but strain *Fusarium tricinctum* showed the highest sensitivity to metabolites of *Bacillus subtilis* I7. *Bacillus amyloliqefaciens* III14 demonstrate the highest activity against mycelium growth of all tested moulds.

Keywords: urea phosphate, *Bacillus* sp., antifungal activity, *Fusarium* sp.

Soil's microorganisms are very important factors which decide about biological processes taking place in the soil. The basic factor modifying soil's quantitative microorganisms composition and its activity is the applied fertilizer. The *urea phosphate* (UP) has a practical application in the food industry, fertiliser industry and environment protection as well. The prior investigations proved that this compound used as the farmyard disinfectant, did not reduce the activity of ammonificators, denitrificators and nitrificators in the soil [1].

Bacillus sp. usually inhabit the soil and are important factor of the natural environment. Strains of many *Bacillus* and relatives possess nitrogenase and are able to

---

[1] Department of Biotechnology and Molecular Biology, Opole University, ul. kard. B. Kominka 6a, 45–035 Opole, Poland, phone: +48 77 401 60 56, email: kgrata@uni.opole.pl

fix atmospheric nitrogen, to increase nutrient availability in the rhizosphere for example phosphorus (*B. megaterium*), to produce of plant growth regulators such as auxin, cytokinins and/or giberelins. Moreover, they may exhibit biological control activity through direct antagonism of the soil-borne fungal and bacterial plant pathogens by metabolize many different bioactive compounds and antibiotics (phospholipides or lipoprotein). From the ecological point of view, natural fungicides are a potential alternative for the use of chemical pesticides, which have a harmful influence on the environment [2–5]. The aim of this study was to estimate the influence of urea phosphate on *Bacillus* sp. population in the soil and the antifungal properties of the *B. subtilis* and *B. amyloliquefaciens* against 4 species of *Fusarium*.

Materials and methods

The studied material consisted of samples brown soil, $\mathrm{pH_{KCl}}$ 5.5, 27, 50 mg $\cdot$ $\mathrm{kg^{-1}}$ soil N-$\mathrm{NO_3}$, 23.80 mg $\cdot$ $\mathrm{kg^{-1}}$ soil N-$\mathrm{NH_4}$, sampled from the layer of soil from 0 to 25 cm in the autumn period. The pot experiment design included four treatments: 1 – control soil, without fertilization, 2 – soil + *farmyard manure* (FYM), 3 – soil + urea phosphate (UP), 4 – soil + urea phosphate + FYM. Soil was watered to 60 % of total water capacity and incubated at a temperature of 20 $^{\mathrm{o}}$C, with moisture content being kept constant over the entire experimental period. Analyses were carried out in three replications, in: day 7 – I term, day 30 – II term and day 90 of the experiment – III term and involved counts of the number of *Bacillus* sp. on DDG medium that consist of (g $\cdot$ $\mathrm{dm^{-3}}$) yeast extract – 3, glucose –10, $\mathrm{K_2HPO_4}$ – 0.5, agar Difco – 20, of soil extract 300 $\mathrm{cm^3}$, distilled water 700 $\mathrm{cm^3}$. The number of *Bacillus* sp. was assayed with the incubation-plate method.

Bacterial strains were selected among a collection of 45 *Bacillus* sp. isolates from samples of soil fertilized with urea phosphate whereas fungal strains from soil fertilized with farmyard manure. Bacterial phenotypic characterization by physiological and biochemical tests were performed according to the Bergey's Manual of Determinative Bacteriology [6] and API 50CHB system (bioMerieux, France). The *Bacillus* were identified as strains of *Bacillus subtilis* – No. B I7, B II11 and *Bacillus amyloliquefaciens* – B III14. They were inoculated into a flask containing 50 $\mathrm{cm^3}$ nutrient broth and incubated at 30 $^{\mathrm{o}}$C for 24 h. Subsequently the 15 $\mathrm{cm^3}$ of nutrient broth was inoculated with a concentrated suspension of *Bacillus* sp. (2.0 OD at $\lambda = 550$ nm) and incubated at 30 $^{\mathrm{o}}$C for various times to give 6, 12, 24 h cultures (working culture). *Fusarium* species were identified according Domsh *et al* [7], Kwasna *et al* [8] and identified as *Fusarium solani* (F5), *Fusarium tricinctum* (F8), *Fusarium oxysporum* (F45), *Fusarium sporotrichoides* (F87). They were cultivated on Czapek-Dox medium (plates and slants) at 25 ± 2 $^{\mathrm{o}}$C for 5–7 days.

The antagonistic activity of the *Bacillus* strains was evaluate on the basis of fungal spore germination and rate index of fungal growth.

Determination of influence of *Bacillus* strains on fungal spore germination. Analysis of the effect of these bacteria on fungal spore germination was performed with the modifying slide germination method. Fungal cultures were cultivated on Czapek-

-Dox slants at 25 ± 2 °C for 7 days and the well-developed fungal culture was rinsed with 10 cm^3 of sterile water containing 0.05 % Tween 80. Mycelium was filtered from sterile gauze and the suspension was adjusted to 10^6 conidia/cm^3 in a hemocytometer. Subsequently 50 mm^3 of working culture of *B. subtilis and B. amyloliqefaciens* and 25 mm^3 of fungal spores were transferred on 1 cm^2 clean glass slides. Conidia germination in broth was used as a control. The slides were incubated in humid chambers in triplicate at 25 ± 2 °C for 24 h. After this period the number of germinated and non-germinated conidia were counted under a microscope using x 200 magnification. Conidia germination was presented as a *rate index of conidia germination* (Ig %) and was obtained using the formula [9]:

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

where: n – the number of germinate spore at a given stage;
a – bonitation scale of the stage: 0 – no germination, 1 – germination hypha length shorter than conidium, 2 – germination hypha length similar to conidium, 3 – germination hypha length was bigger than two lengths of conidium, 4 – germination hypha length was bigger than three or more lengths of conidium and branched;
N – the total number of the macroscopic analysed spores;
4 – the high stage of the scale.

Determination of influence of *Bacillus* strains on mycelium growth. Fungal mycelial-disks (diameter of 10 mm) obtained from growing cultures of test fungal isolates were placed in the centre of Czapek-dox and PDA medium containing 0.5 cm^3 working cultures of *Bacillus* (in four replications). A control was made only with fungal mycelial-disks on both medium. After incubation at 27 °C for 14 days, plates were observed for antifungal activity (at 2 days intervals) and estimated as the rate index of fungal growth (Ifg) using the formula [10]:

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

where: A – the mean from colony measurement,
D – the experiment duration,
$b_1, \ldots, b_x$ – the increase a colony diameter from lasted measurement,
$d_1, \ldots, d_x$ – the number days from lasted measurement.

Statistical calculation were performed by the variance method with the use of Duncan's test.

Results and discussion

The influence of urea phosphate on *Bacillus* growth and antifungal activity of selected *Bacillus* strains was studied. The strong disinfecting proprieties of the urea phosphate were affirmed in earlier investigations. However inhibitory it actions on some microorganisms physiological groups was not noticed.

Changes in the numbers of *Bacillus* sp. in soil are presented in Fig. 1. Among all the treatments, in the presence of urea phosphate (in S + UP as well in S + UP + FYM objects) significant higher count of *Bacillus* sp. was observed when compared with objects containing no urea phosphate or farmyard manure. The highest increase of the number those bacteria after 7 days (206 × 10^3 cfu/g) and 90 days (140 × 10^3 cfu/g) was recorded in fertilized soil (S + UP + FYM). Similarly, the greatest growth of *Bacillus* sp. was observed in non-fertilized soil (S + UP) 125 × 10^3 cfu/g after 7 days and 112 × 10^3 cfu/g after 90 days. Simultaneously, the FYM treatment showed significantly lower value than UP treatments, but significantly higher than in the non-manured soil [1].

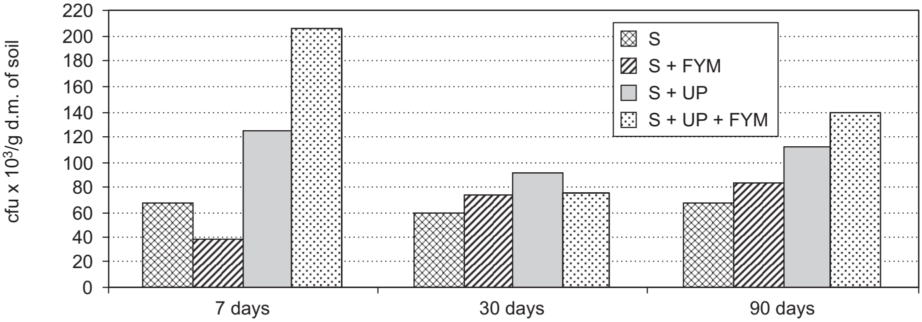

Fig. 1. Number of *Bacilus* sp. in 1 g d.m. of soil depending on fertilization

The antifungal *Bacillus* isolated from fertilized soil was identified as *B. subtilis* (strains BI7 and BII11) and *B. amyloliquefaciens* (BIII14). Members of the *Bacillus* genus and relatives are generally found in soil and most of these bacteria *eg B. subtilis*, *B. cereus*, *B. mycoides*, *B. amyloliquefaciens* are known to suppress several fungal pathogens growth such as *Rhizoctonia* sp., *Sclerotina* sp., *Phytium* sp. [11]. A mechanism by which *Bacillus* sp. suppresses disease is explained in different ways by various authors. Many species of them are capable to produce biologically active substances (*eg* extracellular chitinase) able to disintegrate fungal cell walls [12] as well as growth on the mycelium as a sole carbon source [13]. Some of them (iturin, surfactin) were found to act upon the sterol present in the cytoplasmic membrane of the fungi [14, 15]. *Bacillus subtilis* is one of the major producers of metabolites with antifungal properties in the genus. They possess the activity against some fungi from different taxonomic groups (*eg Penicillium chrysogenum, Aspergillus wentii*, *Trichotecium roseum*, *Botritis cinerea*, *Rhizoctonia solani*) and are even capable of partially controlling a natural infection of plant [4, 16–18]. Some investigators have suggested that biological control or use of microbial fungicides may be an alternative strategy to chemical fungicides [4, 5].

In the present work, antifungal effect of *B. subtilis* and *B. amyloliquefaciens* was determined as the fungal spore germination and the rate index of fungal growth.

The degree of fungal spore germination was different, depending on the strains of *Bacillus* sp. and also age of the culture applied. The results are shown in Table 1.

Table 1

The index rate germination of *Fusarium* (Ig [%] / inhibition of germination [%])

Bacillus strains		*Fusarium solani*	*Fusarium tricinctum*	*Fusarium oxysporum*	*Fusarium sporotrichoides*	Mean
Bacillus subtilis I 7	control	96.69	97.73	97.23	100.00	97.91 c
	6 h	94.11/2.67	78.50/19.68	94.49/2.82	80.00/20.00	86.77 b
	12 h	88.63/8.33	41.66/57.37	93.80/3.53	86.35/13.65	77.61 a
	24h	76.92/20.45	92.22/5.64	84.42/13.17	87.50/12.5	85.26 b
	mean	89.08 b	77.52 a	93.17 c	88.46 b	97.91
Bacillus subtilis II 11	control	96.69	97.73	97.23	100.00	97.91 d
	6 h	93.55/3.25	66.66/31.79	85.7111.85	84.61/15.39	82.63 a
	12 h	95.00/1.75	94,61/3.19	100.00/+2.85	93.38/6.62	95.74 c
	24 h	92.38/4.45	90,527.37	92.70/4.65	95.04/4.96	92.66 b
	mean	94.45 b	87.38 a	93.91 b	93.25 b	92.24
Bacillus amyloliquefaciens III 14	control	96.69	97.73	97.23	100.00	97.91 d
	6 h	95.00/1.75	90.00/7.91	92.46/4.91	100.00/0.0	94.36 c
	12 h	78.9918.30	86.54/11.45	97.17/0.06	100.00/0.0	90.67 b
	24 h	61.11/36.80	97.65/0.08	95.45/1.83	100.00/0.0	88.55 a
	mean	82.94 a	92.98 b	95.57 c	100.00 d	92.87

Small letters – significant difference at the level $p < 0.05$.

In this experiment 6 h, 12 h and 24 h cultures of *Bacillus* sp. were used as an inhibition factor. The strongest inhibition of fungal spore germination was observed when *B. subtilis* I7 was used for 12 h, *B. subtilis* II 11 for 6 h, *B.amyloliquefaciens* for 24 h cultures against all tested fungal strains. *B. subtilis* (strains I7 and II 11) had the highest inhibitory effect for spore germination of *Fusarium tricinctum* (57.37 and 31.79 %, respectively), *B. amyloliquefaciens* for *Fusarium solani* (36.80 %) whereas the spore germination of *Fusarium oxysporum* and *Fusarium sporotrichoides* were weakly inhibited by all of tested *Bacillus* strains. The *B. subtilis* I7 was more efficient than the others *Bacillus* strains.

These observations agree withe the data of some authors, who reported that antifungal metabolites production is strongly conditioned by factors such as strain of the producing microorganisms, age of the culture (growth phase), the chemical composition of the mycelium and the incubation condition [19]. Toure *et al* [18] observed that surfactins were mainly produced during exponential growth with the higher value for cell productivity observed after 12 h. By contrast, iturins and fengycins were mostly synthesized once the culture entered the stationary phase to reach optimal production rate after 72 h. Whereas Feio *et al* [20] showed that synthesis of mycobacilin and bacilysin occurs after the exponential phase of development in *B. subtilis*. Chitarra *et al* [21] detected an antifungal compound produced by a strain of *B. subtilis* that permeabilises fungal spores and blocks germination of *Penicillium roqueforti.* Besides, different sensitivities of the fungi to the various *Bacillus* genus may indicate the production of different metabolites or antifungal products at different concentrations, or both [19].

The antifungal activity of *Bacillus* sp. grown on 2 different media was evaluated towards *Fusarium* sp. as the rate index of fungal growth. The antifungal activity of *Bacillus* strains was dependent on the age of the culture applied and the growth media used. Table 2 shows the results obtained with PDA medium.

Table 2

Effects of the *Bacillus subtilis* and *Bacillus amyloliquefaciens* on *Fusarium* growth on PDA medium (diameter of the mycelium in mm/mycelium growth inhibition in %)

Bacillus strains		*Fusarium solani*	*Fusarium tricinctum*	*Fusarium oxysporum*	*Fusarium sporotrichoides*	Mean
Bacillus subtilis I 7	control	33.03	25.71	34.41	34.01	31.79 c
	6 h	32.00/3.12	27.68/+7.66	32.08/6.77	31.32/7.91	30.81 b
	12 h	32.33/2.12	31.94/+24.23	33.69/2.09	31.06/8.67	32.25 d
	24 h	27.16/17.77	28.69/+11.59	35.16/+2.18	29.54/13.14	30.14 a
	mean	31.14 b	28.55 a	33.83 c	31.48 b	31.25
Bacillus subtilis II 11	control	33.03	25.71	34.41	34.01	31.79 b
	6 h	25.24/23.58	24.14/6.11	25.68/25.37	18.02/47.02	23.27 a
	12 h	25.09/24.04	24.26/5.64	23.68/31.18	19.47/42.75	23.12 a
	24 h	26.29/20.41	26.26/+2.14	24.01/30.22	17.01/49.98	23.38 a
	mean	27.40 c	25.09 b	26.94 c	22.13 a	25.39
Bacillus amyloliquefaciens III 14	control	33.03	25.71	34.41	34.01	31.79 b
	6 h	21.58/34.66	29.06/+13.03	20.06/41.70	14.59/57.10	21.31 a
	12 h	22.34/32.36	25.51/0.78	20.30/41.00	16.06/52.78	20.30 a
	24 h	22.21/32.76	24.43/4.98	20.37/41.80	14.32/57.89	20.35 a
	mean	24.03 b	26.18 b	23.78 b	19.76 a	23.43

Small letters – significant difference at the level $p < 0.05$.

Among the *Fusarium* species, *F. solani, F. oxysporum, F. sporotrichoides* were the most sensitive to metabolites produced by all tested *Bacillus* strains. In case of *F. tricinctum* all the *Bacillus* strains had a very little inhibitory properties and even a small stimulatory properties in case of *B. subtilis* I7 (7.66–24.23 %). It is appear that inhibitory activities of *B. amyloliquefaciens* was significantly higher than all the other *Bacillus* sp., especially towards *F. sporotrichoides* (52.78–57.89 %). A similar influence of *Bacillus* sp. was observed on Czapek-Dox medium. The results are reported in Table 3.

Table 3

Effects of the *Bacillus subtilis* and *Bacillus amyloliquefaciens* on *Fusarium* growth on Czapek-Dox medium (diameter of the mycelium in mm / mycelium growth inhibition in %).

Bacillus strains		*Fusarium solani*	*Fusarium tricinctum*	*Fusarium oxysporum*	*Fusarium sporotrichoides*	Mean
Bacillus subtilis I 7	control	36.62	35.56	36.76	38.31	36.81 d
	6 h	27.98 /23.59	36.47/+2.56	31.94/13.11	30.31/20.88	31.82 b
	12 h	29.41/19.69	36.95/+3.91	27.72/24.59	30.54/20.28	31.15 a
	24h	29.60/19.17	36.78/+3.43	36.76/0.0	29.40/23.26	33.12 c
	mean	30.90 a	36.44 d	33.26 c	32.30 b	33.22
Bacillus subtilis II 11	control	36.62	35.56	36.76	38.31	36.81 c
	6 h	11.33/69.06	34.07/4.19	26.94/26.71	28.03/26.83	25.09 a
	12 h	11.79/67.80	34.43/3.18	26.09/29.03	27.28/28.79	24.90 a
	24 h	25.48/30.42	34.82/2.08	30.06/18.23	26.00/32.13	28.87 b
	mean	21.08 a	34.73 c	29.96 b	29.90 b	28.91
Bacillus amyloliquefaciens III 14	control	36.62	35.56	36.76	38.31	36.81 c
	6 h	17.54/52.10	35.65/+0.25	29.16/20.67	27.46/28.32	27.45 b
	12 h	11.55/68.46	17.99/49.41	28.71/21.90	24.58/35.84	20.70 a
	24 h	25.30/30.91	32.13/9.65	29.60/19.48	22.53/41.19	27.39 b
	mean	22.75 a	30.33 c	31.05 c	28.22 b	28.09

Small letters – significant difference at the level $p < 0.05$.

It was found, that the inhibitory activities of *B. amyloliquefaciens* III 14 and *B. subtilis* II 11 was significantly higher than the *B. subtilis* I7. Growth of *Fusarium solani* and *Fusarium sporotrichoides* was strongly inhibited, whereas growth of *Fusarium tricinctum* was poorly inhibited by all *Bacillus* strain. Among the *Fusarium* species, *F. solani*, *F. oxysporum*, *F. sporotrichoides* were the most sensitive to metabolites produced by *B. amyloliquefaciens* III 14 (6 h and 24 h old culture) whereas *F. tricinctum* was a very little inhibited or a very little stimulated. In contrast to PDA medium, 24 h culture of *Bacillus* sp. exerted the higher inhibiting effect on growth all *Fusarium* species on Czapek-Dox medium.

Conclusion

1. The applied of urea phosphate as the disinfectant of farmyard manure would have the beneficial effect on the increase of the population of *Bacillus* sp. in soil.
2. The inhibitory properties of *Bacillus* species depend on the kind of the ones: age of the culture applied and /or strains of *Bacillus.*
3. *Bacillus subtilis* (strains I 7 and II 11) had the highest inhibitory effect for spore germination of *Fusarium tricinctum* whereas *Bacillus amyloliquefaciens* for *Fusarium solani.*
4. Among the *Bacillus* strains*, B. amyloliqefaciens* had the highest inhibitory properties for mycelium growth of *Fusarium* strains.

5. *Fusarium solani* and *Fusarium sporotrichoides* shows higher sensibility of mycelium to all tested *Bacillus* sp., whereas *Fusarium tricinctum* was a very little inhibited or even stimulated.

6. The present investigations indicated, that urea phosphate is indirectly influenced by plant pathogen increase the number of *Bacillus sp.* with antifungal properies.

References

[1] Grata K, Krzyśko-Łupicka T. Rocz Gleb*,* 2005;LVI(3/4):13-20.
[2] Clanway CP. Plant growth Promotion by Bacillus and Relatives. In: Applications an Systematic of Bacillus and Relatives*.* Berkeley R, Heyndriclex M, Logen N, De Vos P, editors. Miasto: Blackwell Publishing; 2002.
[3] Kerr JR. Microbial Ecology in Health and Disease. 1999;11:129-142.
[4] Marten P, Smalla K, Berg G. J Appl Microbiol. 2000;89:463-471.
[5] Munimbazi C, Bullerman LB. J Appl Microbiol*.* 1998;84:959-968.
[6] Holt JG. Bergey's Manual of Determinative Bacteriology. Baltimore: Williams&Wilkins; 1986.
[7] Domsh KH, Gams W, Anderson TH. Compendium of soil fungi, Miast: Academic Press; 1980.
[8] Kwaśna H, Chełkowski J, Zajkowski P. Grzyby (Mycota). Warszawa-Kraków: PAN; 1991.
[9] Burgieł Z, Kończyk D. Acta Agraria et Silvestria. 1989;XXVIII:5-31.
[10] Burgieł Z. Acta Agraria et Silvestria. 1984;XXIII:187-195.
[11] Sadfi N, Cherif M, Hajlaoui MR, Boudabbous A, Belanger R. Ann Microbiol. 2002;52:323-337.
[12] Wang S-L, Shih I-L, Wang C-H, Tseng K-C, Chang W-T, Twu Y-K, Ro J-J, Wang C-L. Enzyme and Microbial Technol. 2002;31:321-328.
[13] Podile AR, Parcash AR. Can J Microbiol*.* 1996;42:533-538.
[14] Czaczyk K, Trojanowska K, Mueller A. Acta Microbiol Pol. 2002;51:275-283.
[15] Myone AL, Shelby R, Cleveland TE, Tuzun S. J Appl Microbiol*.* 2001;90:622-629.
[16] Földes T, Bánhegyi I, Herpai Z, Varga L, Szigeti J. J Appl Microbiol*.* 2000;89:840-846.
[17] Knox OGG, Killham K., Leifert C. Appl Soil Ecol*.* 2000;15:27-231.
[18] Toure Y, Ongena M, Jacques P, Guiro A, Thonart P. J Appl Microbiol. 2004;96:1151-1160.
[19] Moita C, Feio SS, Nunes L, Curto MJM, Roseiro JC. Int Biodeter Biodegr. 2005;55:261-269.
[20] Feio SS, Barbosa A, Cabriata M, Nunes L, Esteves A, Roseiro JC, Curto MJM. J Industr Microbiol Biotech. 2004;31:195-203.
[21] Chittarra SG, Breeuwer P, Nout RJM, Van Aelst CA, Rombouts MF, Abee T. J Appl Microbiol. 2002;96:159-166.

WPŁYW FOSFORANU MOCZNIKA NA LICZEBNOŚĆ BAKTERII Z RODZAJU *Bacillus* W GLEBIE I AKTYWNOŚĆ PRZECIWGRZYBOWĄ WYBRANYCH SZCZEPÓW NA *Fusarium* sp.

Katedra Biotechnologii i Biologii Molekularnej
Uniwersytet Opolski

Abstrakt: Celem badań była ocena wpływu fosforanu mocznika (FM) na liczebność bakterii z rodzaju *Bacillus* i ocena aktywności fungistatycznej *Bacillus subtilis*, jak również *Bacillus amyloliquefaciens* na *Fusarium* sp. Przeprowadzone badania wykazały korzystne oddziaływanie obiektów z udziałem fosforanu mocznika na liczebność bakterii z rodzaju *Bacillus* sp. W ciągu całego okresu badań liczebność ich była większa niż w glebie nienawożonej i nawożonej obornikiem. Zdolność kiełkowania zarodników grzybów z rodzaju *Fusarium* była hamowana przez *Bacillus* sp., lecz największą wrażliwość na *Bacillus subtilis* I 7 wykazał *Fusarium tricinctum*. Natomiast największą aktywność w stosunku do grzybni wszystkich testowanych grzybów wykazał *Bacillus amyloliquefaciens* III 14.

Słowa kluczowe: fosforan mocznika, *Bacillus* sp., aktywność przeciwgrzybowa, *Fusarium* sp.

DOI: 10.2428/ecea.2012.19(01)019 ECOL CHEM ENG A. 2012;19(1-2):169-176

Iwona ZAWIEJA[1], January BIEŃ[1] and Małgorzata WORWĄG[1]

RECOVERY OF VOLATILE FATTY ACIDS DURING THE PROCESS OF ANAEROBIC STABILIZATION OF SEWAGE SLUDGE COMING FROM THE FOOD INDUSTRY

POZYSKIWANIE LOTNYCH KWASÓW TŁUSZCZOWYCH W PROCESIE STABILIZACJI BEZTLENOWEJ OSADÓW POCHODZĄCYCH Z PRZEMYSŁU SPOŻYWCZEGO

Abstract: The conventional process of oxygen-free stabilization is time-consuming and has low effectiveness. The literature review made, as well as the original studies carried out suggest that the ultrasonic conditioning provides a new way of shortening the duration and increasing the effectiveness of the process of oxygen-free stabilization of sludges forming in the process of treatment of both domestic sewage and industrial liquid wastes. Achieving the considerable increase in the degree of digestion during the oxygen-free stabilization of sludge conditioned with the *ultrasonic* (US) field compared with the reduction of organic matter noted during the oxygen-free stabilization of non-conditioned sludge results from the combined action of both biological hydrolysis, being the first stage of the process, and the phenomenon of sonochemical hydrolysis taking place during the treatment process. Subjecting sludge to conditioning by the method investigated contributes to a considerable intensification of the hydrolysis phase, as reflected by the increase in the production rate and concentration of volatile fatty acids noted in the successive days of conducting the oxygen-free stabilization process, which determines directly the increase of digestion effectiveness, *ie* the degree of sludge digestion and the unit production of biogas. Excessive active sludge formed as a result of the treatment of a mixture of domestic sewage and industrial liquid wastes generated in a plant manufacturing juices and beverages was subjected to oxygen-free stabilization under static conditions. The process was conducted both in laboratory flasks, constituting fermentation chamber models, as well as in a sludge fermentation chamber by Applicon.

Keywords: oxygen-free stabilization, volatile fatty acids, active action of ultrasonic field, biogas

1. Introduction

The Act on Waste of 27 April, 2001, introduces the concept of municipal sewage sludge to refer to the sludge originating from a sewage treatment plant's digestion chambers and other installations used for the treatment of municipal sewage and other

---

[1] Faculty of Environmental Engineering and Protection, Institute of Environmental Engineering, Czestochowa University of Technology, ul. Brzeźnicka 60a, 42–200 Częstochowa, Poland, phone: +48 34 325 73 34 ext. 64, fax: +48 34 34 372 13 04, email: izawieja@is.pcz.czest.pl

wastewater with composition similar to that of municipal sewage, which include wastewater coming, *inter alia*, from [1]: the processing of milk and fruits and vegetables; the production and bottling of soft drinks and alcoholic liquors; meat processing; the production of animal feed from vegetable raw materials; the production of gelatine and glues from animal skin and bones; malt-houses; fish processing; the production of vegetable and animal fats; and sugar factories.

The disposal of sewage sludge on a landfill or its natural utilization should be preceded by transformation processes that will eliminate the noxiousness resulting from their decay, and will prevent the microbial decomposition [2]. The most commonly used process of biochemical sewage sludge stabilization is the methane fermentation process [3]. The methane fermentation process involves the decomposition of macromolecular organic substances by different groups of bacteria into simple compounds, mainly methane and carbon dioxide [3]. The use of methane fermentation results in changes in the composition of the sludge and the gaseous phase [4]. A reduction in organic compounds by approx. 50 % and a decrease in the amount of noxious biological matter have been observed in the methane fermentation process [2]. An important factor in the energy aspect is the amount of energy recovered in the form of volatile fatty acids [5]. The neutralization of sludge by the methane fermentation method is a process that is very advantageous in terms of energy, as it does not require large energy inputs, and the product of reactions occurring in this process is a high-energy biogas [6]. A drawback of this process is a low rate of degradation of organic compounds contained in the sludge [7]. Therefore, the sludge must be subjected to the process of conditioning that enhances directly its susceptibility to biodegradation. A phase limiting the fermentation process is the hydrolytic phase. Increasing the degree of sewage sludge disintegration before the methane fermentation process contributes to the intensification of the hydrolysis process, which results in an increase in the concentration and the rate of increment of volatile fatty acids that form a fermentation semi-product and a substrate for methanogenic bacteria.

2. Experimental

2.1. Testing substrate

The subject of the tests was excessive active sludge coming from the waste treatment plant functioning at the Jurajska Spoldzielnia Pracy works in Myszkow. The tests were conducted on a mixture of excessive and digested sewage sludges that were subjected to mesophyllic methane fermentation, which was periodical in character. The excessive sludge constituted 90 % of the mixture, while the remaining 10 % were made up of digested sludge playing the role of an inoculant.

2.2. Testing methodology

The purpose of the tests was to examined the process of hydrolysis in the oxygen-free stabilization of sewage sludge and to determine the effectiveness of the methane fermentation process. The tests were conducted in a laboratory scale under mesophyllic conditions in ten glass flasks constituting fermentation chamber models. At the same time, tests for the assessment of methane fermentation effectiveness were conducted in a bioreactor by Applicon.

At the first stage, a mixture of digested sludge and non-conditioned excessive sludge, designated as Mixture I, was subjected to 10 days' stabilization. The next stage consisted of the process of stabilization of a mixture of digested sludge and excessive sludge that had been subjected to the active action of an ultrasonic field. In order to determine the best parameters of sludge conditioning, the most advantageous vibration amplitude and sonification time were selected. The criterion for the selection of the parameters sought for was the increase in the concentration of organic matter in the supernatant water of the excessive sludge after sonification, expressed as the COD of the supernatant water. A VC-750 type ultrasonic disintegrator was used for the tests. The following vibration amplitudes were used in the tests: 15.3 μm; 21.4 μm; 30.5 μm; and 36.6 μm; whose action was examined for the sonification time of 30–360 s. At the second stage of tests, based on the performed optimization of the ultrasonic field parameters, Mixture II, *ie* the excessive sludge conditioned with the ultrasonic field of an amplitude of 36.6 μm and an exposure time of 240 s, was subjected to oxygen-free stabilization.

The following physicochemical parameters were determined: pH value using a pH-meter, Model 59002-00, by Cole-Parmer Instrument Company – according to the standard PN-91/C-04540/05 [8]; dry matter, dry organic matter, and dry mineral matter – by the direct gravimetric method according to the standard PN-EN-12879 [9]; *volatile fatty acids* (VFA) – according to the standard PN-75/C-04616/04 [10]; basicity – according to the standard PN-74/C-04540/00 [11]; acidity – according to the standard PN-74/C-04540/00 [12]; *chemical oxygen demand* (COD – Cr), as determined by the chromate method – according to the standard PN-74/C-04578/03) [13]; ammonium nitrogen – according to the standard PN-ISO 5664:2002 [14]; and total nitrogen – according to the standard PN-73/C-04576/14 [15].

3. Test results

A mixture of non-conditioned excessive sludge and digested sludge, playing the role of an inoculant (Mixture I), was subjected to subjected to oxygen-free stabilization. Abrupt changes in the values of selected physicochemical parameters were observed during the tests. Those changes might result from the inhomogeneous structure of the sludges. Excessive sewage sludge is fairly hard to undergo biochemical decomposition under oxygen-free conditions. This is indicated by the degree of sludge fermentation achieved on the tenth day of conducting the process of stabilization of Mixture I. Therefore, on the basis of the performed tests it was found it necessary to subject the sludges to the process of pre-conditioning with the active action of the US field in order to increase the effectiveness of the process.

During the process of methane fermentation of Mixture I conducted in fermentation flasks, an approx. 35 % degree of sludge fermentation was noted. The concentration of volatile fatty acids kept increasing until the sixth day of running the process, when it achieved a value of 805 mgCH$_3$COOH/dm^3. From the sevenths day on, the VFA concentration steadily decreased down to a value of 102 mgCH$_3$COOH/dm^3 on the tenth day of the process. During the oxygen-free stabilization process conducted in the bioreactor, an approx. 43 % degree of sludge fermentation was achieved after 25 days of the process. The analysis of the sludges after 25 days showed that the VFA concentration on the last day of fermentation amounted to 445 mgCH$_3$COOH/dm^3.

At the next stage, excessive sludge conditioned with the ultrasonic field with a vibration amplitude of 36.6 μm and a sonification time of 240 s (Mixture II) was subjected to the process of methane fermentation. In the case of Mixture II, an approx. 40 % degree of sludge fermentation was noted after a period of 10 days' stabilization. The concentration of volatile fatty acids before the oxygen-free stabilization process was 943 mgCH$_3$COOH/dm^3. On the second day of the process, the value of VFA concentration reached its maximum of 171 mgCH$_3$COOH/dm^3. Ultimately, the VFA concentration on the tenth day amounted to 658 mgCH$_3$COOH/dm^3.

In the case of the process conducted in the fermentation chamber for Mixture II, an approx. 56 % degree of sludge fermentation was achieved after 25 days of the process. The concentration of volatile fatty acids on the 25th day of stabilization was 702 mgCH$_3$COOH/dm^3.

Tables 1 and 2 summarize the results obtained from the oxygen-free stabilization conducted in laboratory flasks, while Tables 3 and 4 shows the results obtained during carrying out methane fermentation in the bioreactor for a period of 25 days.

Table 1

The selected physicochemiacal parameters of Mixture I submitted methane fermentation process (laboratory flasks 10-day process)

Indicator/Unit	Time of methane fermentation, d										
	0	1	2	3	4	5	6	7	8	9	10
Dry mass [g/dm^3]	18.3	16.4	16.3	15.8	14.9	14.2	13.5	13.7	13.8	13	12.8
Dry organic mass [g/dm^3]	17.5	15.1	14.8	14	13.2	12.6	11.4	11.6	11.8	11.4	11.1
Dry mineral mass [g/dm^3]	2.2	1.3	1.5	1.8	1.7	1.6	2.1	2.1	2.0	1.6	1.7
Acidity [mval/dm^3]	2.4	4.4	4.8	5.6	5.2	4.8	4.4	5.2	5.2	5.6	5.6
Alkalinity [mg CaCO$_3$/dm^3]	1660	1860	1960	2140	2160	2200	2240	2280	2260	2280	2280
COD [mg/dm^3 O$_2$]	834	1055	1048	1041	862	1120	718	195	181	172	164
Volatile fatty acids (VFA) [mgCH$_3$COOH/dm^3]	360	360	737	720	634	771	805	360	205	154	102
Kjeldahl nitrogen [mg N/dm^3]	302	355	406	436	431	459	464	518	478	504	498
Ammonia nitrogen [mg N-NH$_4^+$/dm^3]	20.1	280	324	364	434	439	448	452	478	503	517
pH	7.68	7.54	7.45	7.42	7.44	7.40	7.38	7.30	7.49	7.47	7.43

Table 2

The selected physicochemiacal parameters
of Mixture I submitted methane fermentation process (laboratory flasks 10-day process)

Indicator/Unit	Time of methane fermentation, d										
	0	1	2	3	4	5	6	7	8	9	10
Dry mass [g/dm^3]	20.3	18.9	18.4	18.3	18	17.1	16.3	15.7	15.6	15.5	14.65
Dry organic mass [g/dm^3]	15.9	15.7	14.6	13.8	13.4	12.9	12.5	11.7	11.0	10.5	9.6
Dry mineral mass [g/dm^3]	4.4	3.2	3.8	4.5	4.6	4.2	3.8	3.6	4.4	4.2	3.55
Acidity [mval/dm^3]	3.6	3.8	4.4	4.5	4.4	4.0	3.2	3.1	3.0	2.9	3.0
Alkalinity [mg CaCO$_3$/dm^3]	1480	1500	1760	2000	2000	2240	2400	2500	2440	2200	2160
COD [mg/dm^3 O$_2$]	1244	3290	3487	2825	2523	2668	1727	938	892	887	975
Volatile fatty acids (VFA) [mgCH$_3$COOH/dm^3]	943	1474	1714	1568	1448	1603	1311	1097	688	651	658
Kjeldahl nitrogen [mg N/dm^3]	319	319	386	439	414	428	476	504	562	586	604
Ammonia nitrogen [mg N-NH$_4^+$/dm^3]	213	224	224	280	336	380	397	403	408	420	420
pH	7.4	7.8	7.87	7.89	7.78	7.86	8.11	8.07	7.93	8.14	7.82

Table 3

The selected physicochemiacal parameters
of Mixture I submitted methane fermentation process (bioreactor-25-day process)

Indicator/Unit	Time of methane fermentation, d	
	0	25
Dry mass [g/dm^3]	17.5	11.5
Dry organic mass [g/dm^3]	15.3	8.7
Dry mineral mass [g/dm^3]	2.2	2.8
Acidity [mval/dm^3]	2.4	3.2
Alkalinity [mg CaCO$_3$/dm^3]	1660	2540
COD [mg/dm^3 O$_2$]	834	708
Volatile fatty acids (VFA) [mgCH$_3$COOH/dm^3]	205	445
Kjeldahl nitrogen [mg N/dm^3]	302	610
Ammonia nitro gen [mg NH$_4^+$/dm^3]	20.1	52.64
pH	7.68	7.7

Table 4

The selected physicochemiacal parameters
of Mixture II submitted methane fermentation process (bioreactor-25-day process)

Indicator/Unit	Time of methane fermentation, d	
	0	25
Dry mass [g/dm^3]	30.3	14.5
Dry organic mass [g/dm^3]	15.9	7.03
Dry mineral mass [g/dm^3]	13.4	5.5
Acidity [mval/dm^3]	3.6	3.9
Alkalinity [mg $CaCO_3$/dm^3]	1480	2630
COD [mg/dm^3 O_2]	1244	814
Volatile fatty acids (VFA) [mgCH_3COOH/dm^3]	943	702
Kjeldahl nitrogen [mg N/dm^3]	319	798
Ammonia nitro gen [mg N-NH_4^+/dm^3]	213	602
pH	7.4	7.37

The tests carried out confirmed the effectiveness of the sonification process as a disintegrating measure that considerably contributes to increasing the susceptibility of sludge to biodegradation. An increase in the rate of hydrolysis was achieved, as reflected by a considerable increase in the concentration of volatile fatty acids in the successive days of conducting the stabilization process, which had a direct effect of extending the time of intensive biogas production.

4. Summary

The preconditioning of excessive sludge with the ultrasonic field had the effect of enhancing the degree of its disintegration. The process of hydrolysis was intensified. An increase in the concentration of volatile fatty acids occurred in the successive days of conducting the process and, in addition, an increase in the degree of sludge fermentation and was noted that an increased biogas production was achieved. The optimal effectiveness of sludge sonification was achieved for an US field vibration amplitude of 36.6 μm and for an exposure time of 240 s. In the case of the oxygen-free stabilization of non-conditioned sludge (Mixture I), the highest value of VFA concentration was noted on the sixth day of conducting the stabilization process. In the case of sludge conditioned with the ultrasonic field with an amplitude of 36.6 μm and for an exposure duration of 240 s (Mixture II), the highest value of VFA concentration was noted already on the second day of conducting methane fermentation. For the mixtures tested, after 25 days of conducting the process, the following sludge fermentation degrees were obtained: Mixture I: 43 %, Mixture II: 56 %, and a unit biogas production of 2.43 dm^3/g d.m.$_{org}$ and 3.54 dm^3/g d.m.$_{org}$, respectively.

Acknowledgement

This work was financially supported by BG-401/403/07.

References

[1] Rozporządzenie Ministra Środowiska z dnia 29 listopada 2002 r. w sprawie warunków jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego (Dz.U.2002.212.1799).
[2] Skalmowski K. Poradnik gospodarowania odpadami, VERLAG DASHOFER, Warszawa: 1999.
[3] Janosz-Rajczyk M, Dąbrowska L, Płoszaj J. Zmiany zawartości metali ciężkich podczas fermentacji metanowej kondycjonowanych osadów ściekowych. Inż Ochr Środow. 2003;6:157-166.
[4] Magrel L. Metodyka oceny efektywności procesu fermentacji metanowej wybranych osadów ściekowych. Białystok: Wyd. Politech. Białostockiej; 2002.
[5] Ying-Chih Chiu, Cheng-Nan Chang, Shwu-Jiuan Huang.Prosimy o podanie inicjałów imion Usprawnienie odzyskiwania lotnych kwasów z poddawanych beztlenowych fermentacji osadów ściekowych, Materiały Konferencyjne nt. Osady ściekowe – odpad czy surowiec?, Częstochowa: Wyd. Politech. Częstochowskiej. 1997;16-24.
[6] Bień JB, Zawieja I. Wpływ alkalicznego kondycjonowania osadów nadmiernych na intensyfikację produkcji biogazu w procesie stabilizacji beztlenowej. Inż Ochr Środow. 2005;8:201-209.
[7] Tiehm A, Nickel K, Neis U. The use of ultrasoud to accelerate the anaerobic digestion of sewage sludge. Water Sci Technol. 1997;36:121-128.
[8] Polskie Normy (PN-91/C-04540/05), Wyd. Normalizacyjne, Warszawa
[9] Polskie Normy (PN-EN-12879), Wyd. Normalizacyjne, Warszawa
[10] Polskie Normy (PN-75/C-04616/04), Wyd. Normalizacyjne, Warszawa.
[11] Polskie Normy (PN-74/C-04540/00), Wyd. Normalizacyjne, Warszawa.
[12] Polskie Normy (PN-74/C-04540/00), Wyd. Normalizacyjne, Warszawa.
[13] Polskie Normy (PN- 74/C-04578/03), Wyd. Normalizacyjne, Warszawa.
[14] Polskie Normy (PN-ISO 5664:2002), Wyd. Normalizacyjne, Warszawa.
[15] Polskie Normy (PN-73/C-04576/14), Wyd. Normalizacyjne, Warszawa.

POZYSKIWANIE LOTNYCH KWASÓW TŁUSZCZOWYCH W PROCESIE STABILIZACJI BEZTLENOWEJ OSADÓW POCHODZĄCYCH Z PRZEMYSŁU SPOŻYWCZEGO

Instytut Inżynierii Środowiska
Politechnika Częstochowska

Abstrakt: Konwencjonalny proces stabilizacji beztlenowej jest często czasochłonny i ma niską efektywność. Dokonany przegląd literaturowy, jak również przeprowadzone badania własne sugerują, że ultradźwiękowe kondycjonowanie stanowi nową drogę do skrócenia czasu oraz zwiększenia efektywności procesu stabilizacji beztlenowej osadów, powstających zarówno w procesie oczyszczania ścieków bytowo-gospodarczych, jak i przemysłowych. Uzyskanie znacznego wzrostu stopnia przefermentowania podczas stabilizacji beztlenowej osadów kondycjonowanych polem ultradźwiękowym (UD), w odniesieniu do redukcji substancji organicznych odnotowanych podczas stabilizacji beztlenowej osadów niepreparowanych, wynika z kombinacji działania zarówno hydrolizy biologicznej, stanowiącej pierwszy etap procesu, jak również zjawiska hydrolizy sonochemicznej, mającej miejsce podczas procesu preparowania. Poddanie osadów kondycjonowaniu badaną metodą wpływa na znaczną intensyfikację fazy hydrolizy, czego wyrazem był odnotowany w kolejnych dniach prowadzenia procesu stabilizacji beztlenowej wzrost tempa produkcji oraz stężenia lotnych kwasów tłuszczowych, warunkujący bezpośrednio zwiększenie efektywności fermentacji, tj. stopnia przefermentowania osadów oraz jednostkowej produkcji biogazu. Stabilizacji beztlenowej, w warunkach statycznych, poddano nadmierny osad czynny powstający w wyniku oczyszczania mieszaniny ścieków bytowo-gospodarczych oraz przemysłowych powstających na terenie zakładu produkującego soki oraz napoje. Proces prowadzono zarówno w kolbach laboratoryjnych, stanowiących modele komór fermentacyjnych, jak również w komorze fermentacyjnej firmy Applicon.

Słowa kluczowe: stabilizacja beztlenowa, hydroliza, lotne kwasy tłuszczowe, kondycjonowanie, czynne działanie pola ultradźwiękowego.

Varia

Invitation for ECOpole ’12 Conference

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 21st annual Central European Conference ECOpole ’12, which will be held in 1113 X 2012 (Thursday–Saturday) at the Conference Center “Rzemieslnik” in Zakopane, PL.

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

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

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format)
- extended Abstracts (4–6 pages) in the semi-annual journal *Proceedings of ECOpole*
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

Additional information one could find on the Conference website:

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15th July 2012** and for the Extended Abstracts: **1st October 2012**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2012**) on the Conference website.

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

At the Reception Desk each participant will obtain abstracts of the Conference contributions as well as the Conference Programme recorded on electronic media (the Programme will be also published on the ECOpole '12 website).

Further information is available from:
Prof. dr hab. eng. Maria Wacławek
Chairperson of the Organising Committee
of ECOpole '12 Conference
Opole University
email: Maria.Waclawek@o2.pl
and mrajfur@o2.pl
phone +48 77 455 91 49 and +48 77 401 60 42
fax +48 77 401 60 51

Conference series

1. 1992 Monitoring '92 Opole
2. 1993 Monitoring '93 Turawa
3. 1994 Monitoring '94 Pokrzywna
4. 1995 EKO-Opole '95 Turawa
5. 1996 EKO-Opole '96 Kędzierzyn Koźle
6. 1997 EKO-Opole '97 Duszniki Zdrój
7. 1998 CEC ECOpole '98 Kędzierzyn-Koźle
8. 1999 CEC ECOpole '99 Duszniki Zdrój
9. 2000 CEC ECOpole 2000 Duszniki Zdrój
10. 2001 CEC ECOpole '01 Duszniki Zdrój
11. 2002 CEC ECOpole '02 Duszniki Zdrój
12. 2003 CEC ECOpole '03 Duszniki Zdrój
13. 2004 CEC ECOpole '04 Duszniki Zdrój
14. 2005 CEC ECOpole '05 Duszniki Zdrój
15. 2006 CEC ECOpole '06 Duszniki Zdrój
16. 2007 CEC ECOpole '07 Duszniki Zdrój
17. 2008 CEC ECOpole '08 Piechowice
18. 2009 CEC ECOpole '09 Piechowice
19. 2010 CEC ECOpole '10 Piechowice
20. 2011 CEC ECOpole '11 Zakopane

GUIDE FOR AUTHORS

A digital version of the manuscript should be sent to:

Prof dr hab. Witold Wacławek,
Editor-in-Chief of Ecological Chemistry and Engineering A
Uniwersytet Opolski
ul. kard. B. Kominka 6
45–032 Opole
Poland
phone +48 77 401 60 42, +48 77 455 91 49
Fax +48 77 401 60 51
email: maria.waclawek@o2.pl
mrajfur@o2.pl

The Editor assumes, that an author submitting a paper for publication has been authorised to do that. It is understood the paper submitted to be original and unpublished work, and is not being considered for publication by another journal. After printing, the copyright of the paper is transferred to *Towarzystwo Chemii i Inżynierii Ekologicznej* (*Society for Ecological Chemistry and Engineering*).

"*Ghostwriting*" and "*guest authorship*" are a sign of scientific misconduct. To counteract them, please provide information, for the Editor, on the percentage contribution of individual Authors in the creation of publications (including the information, who is the author of concepts, principles, methods, etc.). Editorial Board believes that the main responsibility for those statements bears the Author sending the manuscript.

In preparation of the manuscript please follow the general outline of papers published in *Ecological Chemistry and Engineering A*, available on this site; a sample copy can be sent, if requested.

Papers submitted are supposed to be written in English language and should include a summary and keywords, if possible also in Polish language.

Generally, a standard scientific paper is divided into:

– Introduction: you present the subject of your paper clearly, indicate the scope of the subject, present state of knowledge on the paper subject and the goals of your paper;

– Main text (usually divided into: Experimental – you describe methods used; Results and Discussion);

– Conclusions: you summarize your paper;

– References.

The first page should include the author's (authors') given name(s) without titles or scientific degrees like Prof., Ph.D., etc., their affiliations, phone and fax numbers and their email addresses however, with the corresponding author marked by an asterisk.

It is urged to follow the units recommended by the *Systéme Internationale d'Unites* (SI). Graph axis labels and table captions must include the quantity units.

Symbols recommended by the International Union of Pure and Applied Chemistry (Pure and Appl Chem. 1979;51:1-41) are to be followed. Graphics (drawings, plots) should be supplied in the form of digital vector-type files, *eg* CorelDraw v.9, Excel, Inkscape or at least in a bitmap format (TIF, JPG) 600 DPI. In the case of any query please feel free to contact with the Editorial Office. Footnotes, tables and graphs should be prepared as separate files. References cited chronologically should follow the examples given below:

[1] Lowe DF, Oubre CL, Ward CH. Surfactants and cosolvents for NAPL remediation. A technology practices manual. Boca Raton: Lewis Publishers; 1999.

[2] Fasino CR, Carino M, Bombelli F. Oxidant profile of soy standardized extract. In: Rubin R, Stryger CS, editors. Joint Meeting 2001 – Book Abstracts '2001 Year of Natural Products Research'. New York: Harper and Row; 2001.

[3] Wosiński S. Effect of composition and processing conditions of ceramic and polymer composites on the electric field shielding ability [PhD Thesis]. Poznań: Poznan University of Technology; 2010.

[4] Trapido M, Kulik N, Veressinina Y, Munter R. Water Sci Technol. 2009;60:1795-1801. DOI: 10.2166/wst.2009.585.

[5] Cañizares P, Lobato J, Paz R, Rodrigo MA, Sáez C. Chemosphere. 2007;67:832-838. DOI: 10.1016/j.chemosphere.2006.10.064.

[6] Hakala M, Nygård K, Manninen S, Huitari S, Buslaps T, Nilsson A, et al. J Chem Phys. 2006:125:084504-1-7. DOI: 10.1063/1.2273627.

[7] Simeonov D, Spasov L, Simeonova P. Statistical calibration of model solution of analytes. Ecol Chem Eng A. Forthcoming 2012.

Journal titles should preferably follow the Chem. Abst. Service recommended abbreviations.

Each publication is evaluated by at least two independent reviewers from outside of the unit.

Receipt of a paper submitted for publication will be acknowledged by email. If no acknowledgement has been received, please check it with the Editorial Office by email, fax, letter or phone.

REDAKTOR TECHNICZNY
Halina Szczegot

SKŁAD I ŁAMANIE
Jolanta Brodziak

PROJEKT OKŁADKI
Jolanta Brodziak

Druk: „Drukarnia Smolarski”, Józef Smolarski, 45–326 Opole, ul. Sandomierska 1. Objętość: ark. wyd. 14,25, ark. druk. 11,75 Nakład: 350 egz. + 5 nadb. aut.