SOCIETY OF ECOLOGICAL CHEMISTRY AND ENGINEERING

ECOLOGICAL CHEMISTRY AND ENGINEERING A

CHEMIA I INŻYNIERIA EKOLOGICZNA A

Vol. 20 No. 4-5

OPOLE 2013

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Wersją pierwotną czasopisma jest wersja elektroniczna

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

ISSN 1898–6188

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DOI: 10.2428/ecea.2013.20(04)041 ECOL CHEM ENG A. 2013;20(4-5):443-436

Jacek GRZYB[1*] and Krzysztof FRĄCZEK[1]

BIOAEROSOL-FORMING ACTINOMYCETES AT THE SELECTED SITES OF KRAKOW

PROMIENIOWCE TWORZĄCE BIOAEROZOL W WYBRANYCH MIEJSCACH KRAKOWA

Abstract: Krakow is a city where, due to mostly so-called low-stack emissions and intensified traffic, air dustiness continues to increase and often, especially in winter, the threshold values of dustiness are exceeded. Air dustiness increases the number of airborne microorganisms, as they are associated with particles of dust to form bioaerosols. Actinomycetes are one of the most significant components of bioaerosol. Their presence in bioaerosol is dangerous to human health, since even very low concentrations of these microorganisms can cause allergic reactions.

The aim of this study was to verify the relationship between the concentration of actinomycetes in the air of Krakow depending on spatial variation of thermal conditions and the degree of air dustiness. The study was conducted using a cascade impactor for bioaerosol particle separation, including the respirable fraction. Moreover, the measurements of air dustiness were performed simultaneously, separating 4 dust fractions. The research was conducted over 12 months (full calendar year) and the measurements were performed once per month, within one day, at 16 research sites.

The lowest average numbers of actinomycetes were recorded in places characterized by little urban green space (*eg* Main Square or crossroads). On the other hand, the highest numbers were found in green areas (*eg* Blonia Park meadows, green area at the Krakow University of Technology).

Based on the normative classification of air quality (Polish Standard PN-89/Z-04111/02) the number of actinomycetes in 75 % measurements showed that the air was polluted, including heavily polluted air in 16 % measurements.

The most common actinomycetes belonged to the genus *Streptomyces* (*St. albus, St. badius, St. globisporus*).

Keywords: actinomycetes, bioaerosol, air dustiness, Krakow

Actinomycetes acquired the unique ability to colonize the so-called solid surfaces. They can survive on rocks, plants, animals, clothing, food and other bare surfaces. This is due to the properties of their spores, which are resistant to long periods of drying and capable of survival at low moisture content of the substrate on which they grow [1].

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Actinomycetes are one of the important components of bioaerosol. Actinomycetes, mostly in the form of spores, have been identified in the air for a few decades. Until now, the mechanism of their release into the atmosphere has not been fully understood. It is suggested that they can be released into the air as a result of mechanical damage to surface on which they grow, *eg* during agrotechnical operations or strong wind they can be raised from soil surface, in which they develop extensively. Due to their smaller size, it is more difficult for actinomycete spores to transform into bioaerosol phase than for fungal spores [1, 2].

The share of actinomycete spores significantly increases in the bioaerosol fraction below 3.3 μm [3].

The airborne spores of at least several actinomycete species (*eg Streptomyces albus*) have proven their allergic effects. Research has shown that actinomycete spores stimulate macrophages in the lungs, resulting in inflammation and tissue damage [4, 5].

Dusts have also a large share in atmospheric pollution. They originate in the processes of combustion of solid fuels (municipal and household sector), liquid fuels (car engines), in industrial processes and in natural phenomena (*eg* volcanic eruptions). Dust particles with a diameter below 10 micrometers are considered as one of the most toxic components of air; therefore in the European Union dust PM 10 is currently the primary indicator of air quality [6].

Krakow is a city, where due to mostly so-called low-stack emissions and intensified traffic, air dustiness continues to increase and often, especially in winter, the threshold values of dustiness are exceeded. Air dustiness stimulates the increase in the number of airborne microorganisms, since they associate with dust particles to form bioaerosol [7].

The aim of this study was to verify the relationship between the concentration of airborne actinomycetes in Krakow, spatial variability of thermal conditions and the air dustiness level.

Material and methods

The study was conducted over 12 months (full calendar year) during the period from March 2010 to February 2011 in order to detect both the changes in temperature and in the quantitative and qualitative composition of microflora between the seasons of the year – once per month, during one day, at 16 research sites. At the same time, dustiness and microclimatic parameters (temperature, atmospheric pressure, wind energy, relative humidity) were measured at the designated sites to correlate all measured values.

The research sites were selected based on the deviations from the mean annual temperature in Krakow, including:

– 7 sites characterized with temperatures below the average temperature in Krakow,

– 7 sites, where the temperature is above the average,

– 2 sites, which the results from the above-mentioned sites were related to: the first one, with the temperature equal to the average recorded in Krakow and the second one: control site outside Krakow (Table 1).

Table 1

Comparison of research sites

Control site (outside Krakow) (C)	
C	Control site Libertow – 400 m from the “Zakopianka” road – above the basin, where Krakow is located
The research sites with temperatures below the average temperature in Krakow (B1–B7)	
B1	The Kosciuszko Mount – at the top of the Mount
B2	The Krakus Mount – at the top of the Mount
B3	The Nowa Huta Centre of Culture
B4	Blonia Park – in the middle of Blonia Park
B5	Vistula Czerwienski Boulevard – next to the Wawel Dragon
B6	Water reservoir in Nowa Huta – Bulwarowa Street
B7	Botanical Garden – Kopernika Street
The research site in which temperature is equal to the average temperature in Krakow (AVG)	
AVG	The School of Sports Championship area
The research sites with temperatures above the average temperature in Krakow (A1–A7)	
A1	Krakow University of Technology, Jan Paweł II Street – by the new building
A2	Nearby the crossing with Fabryczna Street
A3	The Teatralne Estate in Nowa Huta – behind the building of The Ludowy Theatre at Obroncow Krzyza Street
A4	Main Market Square – nearby the Town Hall Tower
A5	Mickiewicza Avenue – between the University of Agriculture and the AGH – University of Science and Technology
A6	ArcelorMittal Poland – Ujastek Street – in front of the administrative building
A7	ArcelorMittal Poland – Igolomska Street, nearby the crossing with Dymarek Street

The air samples were collected using a 6-stage Graseby-Andersen impactor. Application of this instrument allowed for the separation of the examined bioaerosol particles depending on their aerodynamic diameters into fractions: over 7.0 μm, 7.0–4.7 μm, 4.7–3.3 μm, 3.3–2.1 μm, 2.1–1.1 μm, and 1.1–0.65 μm. The term respirable fraction means the total number of bacteria from fractions below 4.7 μm [8, 9]. The sampling lasted 5 minutes; the air flow through the impactor was 28.3 dm^3 per minute. The Gauze’s medium was applied and the incubation was carried out for 7 days at 28 ^{o}C to isolate actinomycetes. Dustiness and microclimatic parameters were measured simultaneously to correlate the measured values. Dust concentration measurements were performed with a DustTrak II Aerosol Monitor 8530 (TSI Inc.) which operates based on laser photometry (measurement time is 60 seconds – for each fraction). In this research project, the dust concentration was measured simultaneously for 4 dust fractions: PM10, PM4, PM2,5 and PM1. The PM10 dust is composed of solid and liquid particles suspended in the air, both of organic and inorganic substances. The suspended dust may contain toxic substances, such as policyclic aromatic hydrocarbons (*eg* benzo-α-pyrene), heavy metals, dioxins and furanes as well as microorganisms deposited on solid and liquid particles. Dust measured as PM4 is the fraction of respirable dust, which corresponds to the respirable fraction with the aerodynamic diameter below 4.7 μm measured using a cascade impactor. Kestrel 4000 Pocket Weather Meter (Nielsen-Kellerman) was applied to determine the microclimatic parameters (temperature, wind energy and relative humidity).

The correlation between the examined factors was analyzed using Statistica 9.1 software.

Results and discussion

Actinomycetes form a group of microorganisms, which normally occurs in the air in much lower concentrations than bacteria and fungi, but their comparable quantities can cause much more serious health effects. The number of actinomycetes was 20 % higher at a control site outside than within Krakow. The average actinomycete bioaerosol concentration at the sites with temperature below the mean (indicated in Table 1 as B) was 66 CFU $\cdot$ m^{-3}, at the control site (marked as C) located outside Krakow it was 61 CFU $\cdot$ m^{-3}, at the site with average temperature (AVG) – 60 CFU $\cdot$ m^{-3} and at the sites with temperature above the average (A) – 56 CFU $\cdot$ m^{-3}. If assumed that B equals 100 %, the percentages amount to: C – AVG – A: 92.5 % – 90.9 % – 84.8 %, respectively. This means that the numbers of this microbial group were about 15 % lower at the sites with temperature above the average (Table 2).

Table 2

Comparison of minimum, maximum, average and total numbers of actinomycetes [CFU $\cdot$ m^{-3}]

Research site	Minimum	Mean	Maximum	The sum of annual measurements
C	0	**61**	212	733
B1	14	72	488	858
B2	0	51	127	616
B3	0	66	262	787
B4	9	99	665	1193
B5	0	49	290	583
B6	0	63	219	760
B7	0	86	361	1037
Mean from **B1–B7**		**66**		
AVG	0	**60**	290	718
A1	18	110	431	1322
A2	0	26	64	316
A3	7	62	290	742
A4	7	32	99	385
A5	0	41	177	495
A6	0	64	332	768
A7	0	57	375	689
Mean from **A1–A7**		**56**		

Table 3

Comparison of the number of actinomycetes at the research sites during the entire study period with the determination of microbial air pollution according to the Polish Standard PN-89/Z-04111/02 [CFU · m^{-3} of air]

Research sites	Measurement period												Measurements when the air was polluted [%]	Including heavily polluted [%]
	03.’10	04.’10	05.’10	06.’10	07.’10	08.’10	09.’10	10.’10	11.’10	12.’10	01.’11	02.’11		
C	**7**	**99**	**57**	**0**	**71**	**212**	**185**	**21**	**35**	**18**	**0**	**28**	75.0	16.7
B1	**28**	**14**	**28**	**14**	**85**	**488**	**44**	**35**	**44**	**18**	**18**	**42**	100.0	8.3
B2	**85**	**64**	**14**	**0**	**120**	**127**	**9**	**28**	**97**	**26**	**18**	**28**	83.3	16.7
B3	**21**	**35**	**71**	**71**	**78**	**262**	**150**	**28**	**0**	**18**	**26**	**28**	91.7	16.7
B4	**21**	**14**	**21**	**148**	**156**	**665**	**35**	**28**	**18**	**9**	**35**	**42**	91.7	25.0
B5	**35**	**14**	**85**	**21**	**57**	**290**	**18**	**7**	**18**	**0**	**18**	**21**	83.3	8.3
B6	**0**	**7**	**28**	**71**	**198**	**219**	**44**	**92**	**62**	**18**	**0**	**21**	75.0	16.7
B7	**78**	**7**	**7**	**148**	**361**	**346**	**9**	**0**	**0**	**9**	**44**	**28**	50.0	25.0
AVG	**28**	**0**	**7**	**7**	**113**	**290**	**158**	**14**	**0**	**18**	**62**	**21**	66.7	25.0
A1	**21**	**28**	**134**	**191**	**431**	**346**	**44**	**21**	**18**	**18**	**26**	**42**	100.0	33.3
A2	**0**	**21**	**28**	**35**	**57**	**64**	**26**	**7**	**9**	**26**	**35**	**7**	66.7	0.0
A3	**42**	**21**	**49**	**7**	**106**	**290**	**18**	**64**	**88**	**9**	**26**	**21**	83.3	16.7
A4	**7**	**7**	**35**	**7**	**49**	**99**	**9**	**21**	**53**	**53**	**9**	**35**	58.3	0.0
A5	**21**	**0**	**7**	**28**	**134**	**177**	**0**	**28**	**53**	**0**	**18**	**28**	66.7	16.7
A6	**14**	**0**	**28**	**0**	**276**	**332**	**35**	**21**	**35**	**26**	**0**	**0**	66.7	16.7
A7	**156**	**7**	**7**	**7**	**7**	**375**	**0**	**42**	**0**	**35**	**53**	**0**	41.7	16.7

Legend: air pollution levels with actinomycetes according to Polish Standard PN-89/Z-04111/02

< 10 Unpolluted air
10–100 Average air pollution
> 100 Heavy air pollution

The lowest average numbers of actinomycetes were recorded in places characterized by little urban green space (*eg* Main Square or crossroads). On the other hand, the highest numbers were found in green areas (*eg* Blonia Park meadows, green area by the Krakow University of Technology) (Table 2).

Regarding the classification of air quality based on the Polish Standard PN-89/Z-04111/02 (Table 3) the number of actinomycetes exceeded the admissible values in 144 of 192 conducted measurements, which constitutes 75 %, of samples which were considered to be polluted, including 16 % of the measurements, when the air was heavily polluted.

Table 4

Average number of actinomycetes in different seasons of the year [CFU · m^{-3}]

Research site	Spring	Summer	Autumn	Winter
C	9	16	13	3
B1	4	33	7	4
B2	9	14	7	4
B3	7	23	10	4
B4	3	54	5	5
B5	7	20	2	2
B6	2	27	11	2
B7	5	48	0	5
AVG	2	23	10	6
A1	10	54	5	5
A2	3	9	2	4
A3	6	22	9	3
A4	3	9	5	5
A5	2	19	5	3
A6	2	34	5	1
A7	9	22	2	5
Average for research sites B1–B7+A1–A7+AVG	5	27	6	4

Table 5

Percentage of fractions, including the respirable fraction of actinomycetes

Fraction [μm]	The sum of microorganisms from all research sites and year-long measurements [CFU · m^{-3}]	% share of fraction
0.65–1.1	561	4.7
1.1–2.1	1055	8.8
2.1–3.3	2302	19.2
3.3–4.7	3360	28.0
4.7–7.0	3116	26.0
> 7.0	1608	13.4
Share of the respirable fraction		60.6

Table 6

The predominant airborne actinomycete species

Actinomycete species	**C**	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**AVG**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**	Frequency of the species occurrence
Streptomyces albo-griseus			+		++	+				+++	+					+	**9**
Streptomyces albus	+	+++	+		+	+	++	+	++	++		+++	+		+	+	**20**
Streptomyces anulatus	+			++				+			+		+		+		**7**
Streptomyces badius	++		+		++	++			+	++		+	+	++		+	**15**
Streptomyces collinus		++		+				++			+			++			**8**
Streptomyces fradiae					+	+		++	++				+		+	++	**10**
Streptomyces globisporus	++				+		+	+++		++	+	+		+	++		**14**
Streptomyces lavendulae		++	+	++			+	+				+					**8**
Streptomyces longisporus	++		+	+	++		++	+	+	+					+	+	**13**
Streptomyces mirabilis		++	+				+					+					**5**
Streptomyces roseogriseolus					+				+	+					+	+	**5**
Streptomyces sp.		+			+					+							**3**
Streptomyces violaceus-niger				+	+		+			+					+		**5**
Streptosporangium sp.				+				+									**2**

Legend: C, B1, B2 – research sites, as in Table 1.
Frequency of the occurrence of a species (strain): +++ very frequently, ++ frequently, + rarely.

Considering seasons, the average numbers of actinomycetes (Table 4) at the research sites (B1–B7, AVG and A1–A7) rank in the following order: summer (27 CFU · m^{-3}), autumn (6 CFU · m^{-3}), spring (5 CFU · m^{-3}) and winter (4 CFU · m^{-3}).

Table 5 presents total numbers of actinomycetes measured during the year at all research sites to estimate the shares of different bioaerosol fractions. The fraction with the smallest aerodynamic diameter (0.65–1.1 μm) took the lowest share – 4.7 %, while the fraction with the greatest diameter (3.3–4.7 μm) – 28 %. The share of the respirable fraction of actinomycetes was 60.6 %.

A total of 40 strains were isolated, which were subsequently classified into 2 genera – the vast majority of species belonged to the genus *Streptomyces*. Within the genus *Streptomyces* the isolates were classified into 12 species. The most frequently occurring species were: *Streptomyces albus, St. badius* and *St. globisporus.* Strains of the genus *Streptosporangium* could not be assigned to any of the species (Table 6).

A strong correlation was found between temperature and the abundance of actinomycetes from the fraction 2.1–7.0 μm. On the other hand, there was a negative correlation between air humidity and all actinomycete fractions above 1.1 μm. A statistically significant correlation was observed between dust fractions PM2.5 and PM1 and bioaerosol forming actinomycete fractions from 2.1 to 7.0 μm (Table 7).

Table 7

Correlations between the number of actinomycetes and microclimatic factors and dust concentration

Factors	Actinomycetes – fractions					
	>7.0	4.7–7	3.3–4.7	2.1–3.3	1.1–2.1	0.65–1.1
Air temperature	**0.22**	**0.49**	**0.46**	**0.45**	0.35	**0.11**
Relative humidity	**–0.18**	**–0.43**	**–0.44**	**–0.43**	**–0.32**	–0.01
Wind energy	–0.06	–0.09	–0.11	–0.07	–0.05	**0.04**
Dust – fraction PM10	–0.05	0.09	**0.15**	0.07	–0.03	–0.11
Dust – fraction PM4	–0.10	0.07	0.12	0.06	0.00	–0.09
Dust – fraction PM2.5	–0.07	**0.18**	**0.24**	**0.15**	0.02	**–0.14**
Dust – fraction PM1	–0.08	**0.14**	**0.18**	**0.17**	–0.02	–0.13

Legend: bolded – results significant at $p < 0.01$.

Conclusions

Based on the year-long study, conducted from March 2010 to February 2011 at 15 research sites in Krakow and one control site outside Krakow, the following conclusions may be drawn:

1. Based on the normative classification of air quality (Polish Standard PN-89/Z-04111/02) the number of actinomycetes showed that the air was polluted in 75 % of measurements, 16 % measurements, when heavy pollution of the air was detected.

2. Particles of the respirable fraction – with the aerodynamic diameter in the range 3.3–4.7 μm represented the most numerous group, the share of fraction 2.1–3.3 μm was

less numerous. The smallest number of microorganisms was detected in the extreme fractions (below 1.1 μm and above 7 μm).

3. The following statistically significant correlations were found:

– positive between temperature and the number of actinomycetes,

– negative between the number of actinomycetes and air humidity,

– positive between actinomycetes from the fractions 2.1–7 μm and dust with the diameter below 2.5 μm (PM2.5 and PM1).

4. Actinomycetes of the genus *Streptomyces* were most frequently observed (*St. albus, St. badius, St. globisporus*).

5. Green urban spaces nearby the Krakow University of Technology and at the Kosciuszko Mount were most heavily contaminated with actinomycete spores.

6. Significant differences in microbial numbers were recorded between research sites with low and high average air temperature. There was a negative correlation between actinomycete numbers and the average air temperature – in "cold" locations (B) the numbers of these microorganisms was from 13 to 15 % higher than in other sites.

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PROMIENIOWCE TWORZĄCE BIOAEROZOL W WYBRANYCH MIEJSCACH KRAKOWA

Katedra Mikrobiologii
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Abstrakt: Kraków jest miastem, w którym głównie na skutek tzw. niskiej emisji oraz wzmożonego ruchu kołowego zapylenie powietrza wciąż wzrasta i nierzadko szczególnie w okresie zimowym są przekraczane progowe wartości zapylenia. Zapylenie powietrza wpływa na zwiększenie się ilości drobnoustrojów w powietrzu, gdyż te ostatnie wiążą się z cząstkami pyłów, tworząc bioaerozol. Jednym z ważnych składników bioaerozolu są promieniowce. Ich obecność w bioaerozolu jest groźna dla zdrowia ludzkiego, gdyż nawet ich bardzo niskie stężenia mogą działać alergizująco.

Celem niniejszych badań była weryfikacja zależności pomiędzy stężeniem promieniowców w powietrzu na obszarze Krakowa, przestrzennym zróżnicowaniem stosunków termicznych oraz stopniem zapylenia powietrza.

Do badań użyto impaktora kaskadowego w celu uzyskania rozdziału cząstek bioaerozolu, w tym frakcji respirabilnej. Jednocześnie wykonywane były pomiary stopnia zapylenia z podziałem na 4 frakcje. Badania były wykonywane przez 12 miesięcy (pełen rok kalendarzowy), raz w miesiącu, w ciągu jednego dnia, na 16 stanowiskach pomiarowych.

Najniższe średnie liczebności promieniowców notowano w miejscach, gdzie jest mało zieleni (np. Rynek Główny, czy też skrzyżowanie ulic). Najwyższe liczebności stwierdzono na terenach zielonych (np. Błonia, teren zielony przy Politechnice Krakowskiej).

Promieniowce zgodnie z klasyfikacją jakości powietrza atmosferycznego (Polska Norma PN-89/Z-04111/02) powodowały, że w przypadku 75 % wykonanych pomiarów powietrze było zanieczyszczone, w tym silnie zanieczyszczone dla 16 % pomiarów.

Najczęściej stwierdzano występowanie promieniowców z rodzaju *Streptomyces* (*St. albus, St. badius, St. globisporus*).

Słowa kluczowe: promieniowce, bioaerozol, zapylenie, Kraków

DOI: 10.2428/ecea.2013.20(04)042 ECOL CHEM ENG A. 2013;20(4-5):453-460

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COMPUTATIONAL FLUID DYNAMIC METHOD IN COAL COMBUSTION MODELING: POLLUTANTS FORMATION IN AIR AND OXY ATMOSPHERE

ZASTOSOWANIE NUMERYCZNEJ MECHANIKI PŁYNÓW W MODELOWANIU SPALANIA WĘGLA W ATMOSFERZE POWIETRZA I OXY

Abstract: Despite the fact that alternative energy sources sector has been rapidly developed since last years, coal combustion as a major fossil-fuel energy resource (especially in Poland) will continue being a major environmental concern for the next few decades. To meet future targets for the reduction of toxic and greenhouse gases emission new combustion technologies need to be developed: pre-combustion capture, post-combustion capture, and oxy-fuel combustion (the process of burning a fuel using pure oxygen instead of air as the primary oxidant). This paper deals with the air-fried and oxy-fuel hard and brown coal combustion (pulverized coal) combustion, and its impact on pollutants (NO_x and SO_2) formation.

For CFD modeling of media flows and hard and brown coal combustion process the laboratory model of combustion reactor was applied. The material input was set based on technical-elementary analysis of pulverized coal used in experiment and sieves grain-size analysis. Boundary conditions (media flows intensities and temperatures). was set based on laboratory experimental measurements. Radiation case-sensitive WSGGM model (weighted – sum – of – gray – gases model) was used for calculation. The modeling was proceed for different combustion parameters in air and OXY atmosphere in oxygen/fuel ratio variation and fuel humidity variation function. The results was presented in tables and in figures

Keywords: CFD modeling, coal combustion, radiation model, hard coal, brown coal

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Introduction

The role of coal as an energy source has attracted renewed interest due to the stability of its supply and its relatively low cost, which will probably guarantee its inclusion in the energy mix in the foreseeable future [1, 2]. However, coal combustion produces a large amount of CO_2, which is the chief contributor to global climate change. To meet future targets for the reduction of greenhouse gas emissions, CO_2 must be captured and stored [2]. Oxy-coal combustion is a carbon abatement technology that can be used for the capture of carbon dioxide (CO_2) from coal-fired power plants. the amount of unburnt carbon or the Loss on Ignition (LOI) depends on the particle residence time in the furnace, the temperature and the availability of oxygen along the particle path [3].

Considerable knowledge of the fundamentals of heat and mass transfer, combustion processes and pollutant formation under CO_2 – rich conditions has been acquired through extensive experiments and modeling efforts in recent years. However, many fundamental issues remain uninvestigated [4]:

– Oxy-combustion characteristics of different coal types;

– Models for sub-processes (models for devolatilization, char formation, agglomeration and coal group combustion under the oxy-combustion conditions are mostly based on air combustion studies);

– Scaling characteristics of oxy-combustion;

Pressure effect (when operating under elevated pressure, the gas phase flowfield and coal particle residence time may change significantly).

An important issue of implementation this technology is also its impact on problem of pollutants formation, *ie* thermal NO_x due to the absence of nitrogen gas in the combustion atmosphere and SO_2 formation from contaminated fossil fuel.

The authors presents results of simulation witch aim was investigation of NO_x and SO_2 forming during hard and brown coal combustion process in the laboratory reactor using numerical tools.

Methodology

For CFD modeling of media flows and coal combustion process the laboratory model of combustion reactor was applied. The material input was set based on technical-elementary analysis of pulverized coal used in experiment and sieves grain-size analysis. Boundary conditions (media flows intensities and temperatures). was set based on laboratory experimental measurements. Radiation case-sensitive WSGGM model (weighted – sum – of – gray – gases model) was used for calculation. The modeling was proceed for different combustion parameters in air and OXY atmosphere in oxygen/fuel ratio variation and fuel humidity variation function.

Boundary conditions

In Table 1 the results of technical-elementary analysis of applied fuel are presented.

Table 1

Technical-elementary analysis of applied fuel (pulverized hard and brown coal)

Coal proximate analysis	Hard coal	Brown coal
Moisture content [wt. %]	13.23	7.22
Ash [wt. %, db]	4.96	16.2
V.M. [wt. %, db]	30.64	70.0
F.C. [wt. %. db]	51.17	6.58
Heating value [MJ/kg, db]	25.5	19.2
Ultimate analysis [wt. %, daf]		
C	73.60	66.6
H	5.26	6.50
N	1.44	0.74
S	0.80	0.18
O	18.9	26.0
Sieves grain-size analysis: fraction [%]		
< 63 μm	34.08	28.05
63–80 μm	26.51	11.58
80 μm – 0.106 mm	25.29	15.15
0.106 mm–0.160 mm	7.39	36.02
> 0.2 mm	6.73	9.2

Five lambda coefficient value (λ: 0.83; 1.0; 1.1; 1.3; 1.35) and four values of humidity (φ: 0, 7, 14, 21) was chosen to the modeling.

Results

The results was presented in tables and in figures below.

Simulation of hard coal combustion process

In Table 2 the simulation results for hard coal are presented for each lambda value and humidity function.

In Fig. 1 the chosen results of particular exhaust gases components concentrations are presented in lambda coefficient function on example of 7 % humidity content in the fumes.

Combustion process in OXY atmosphere caused almost 70 % increase in dicarbon oxide concentration. The highest values was observed during the fuel combustion in 20/80 oxy-atmosphere, the insignificant decrease (~8 %) of CO_2 concentration was noticed for all oxy-coal combustion processes. The oxygen share increase in OXY-combustion caused few-percent CO_2 concentration reduction.

Table 2

Simulation results for pulverized hard coal combustion: NO_x, SO_2, CO_2, O_2 concentrations in λ and humidity function

	NO_x [ppm]				SO_2 [ppm]				CO_2 [% vol.]				O_2 [% vol.]			
φ. %	0	7	14	21	0	7	14	21	0	7	14	21	0	7	14	21
λ	air															
0.83	0	0	9	87	1545	1453	1400	1308	16.9	16.9	16.5	14.9	0	0	0.1	1.8
1.00	53	75	114	255	1321	1251	1177	1104	16	14.9	14	12.9	1.3	2.4	3.4	4.4
1.10	104	137	229	290	1219	1157	1091	1019	14.7	13.8	13	12.1	2.9	3.8	4.6	5.5
1.20	163	208	288	367	1123	1068	1007	942	13.4	12.7	11.9	11.1	4.4	5.11	5.9	6.8
1.35	288	342	400	430	1012	957	902	844	11.9	11.4	10.6	10	6.2	6.7	7.6	8.2
λ	OXY 20/80															
0.83	40	54	72	100	1139	1087	1015	953	90.3	88.6	86.9	85.1	1.9	3.1	4.2	5.5
1.00	81	93	150	190	955	904	852	799	87.7	86.4	85	83.5	5.8	6.6	7.6	8.6
1.10	132	175	204	215	880	835	786	738	86.6	85.3	84	82.8	7.4	8.2	9.2	9.8
1.20	154	194	232	300	812	768	725	680	85.7	84.5	83.3	82.1	8.7	9.6	10.4	11.2
1.35	193	267	297	304	726	688	649	609	84.5	83.5	82.4	81.4	10.5	11.2	11.9	12.6
λ	OXY 25/75															
0.83	45	55	88	119	1156	1096	1033	970	84.6	83.2	81.4	79.6	7.6	8.5	9.8	11
1.00	84	124	143	185	971	921	868	813	82.1	80.7	79.5	77.9	11.4	12.4	13.1	14.1
1.10	117	142	192	256	895	849	800	750	81.1	79.8	78.6	77.3	12.9	13.7	14.5	15.4
1.20	147	209	242	287	825	782	738	691	80.1	79	77.8	76.6	14.4	15.1	15.9	16.6
1.35	198	258	289	346	738	700	660	619	78.9	77.9	76.8	75.7	16.2	16.8	17.6	18.2
λ	OXY 30/70															
0.83	52	62	83	117	1175	1114	1051	984	79.4	77.7	76.2	74.5	12.8	14.1	15	16.2
1.00	90	126	152	205	987	935	882	826	76.8	75.5	74.1	72.7	16.8	17.6	18.5	19.4
1.10	119	176	209	232	909	862	813	762	75.7	74.5	73.2	71.9	18.3	19.1	19.9	20.7
1.20	138	199	262	300	838	794	749	702	74.7	73.5	72.4	71.2	19.8	20.6	21.3	22
1.35	214	276	326	390	749	710	670	627	73.4	72.4	71.4	70.3	21.7	22.3	22.9	23.6

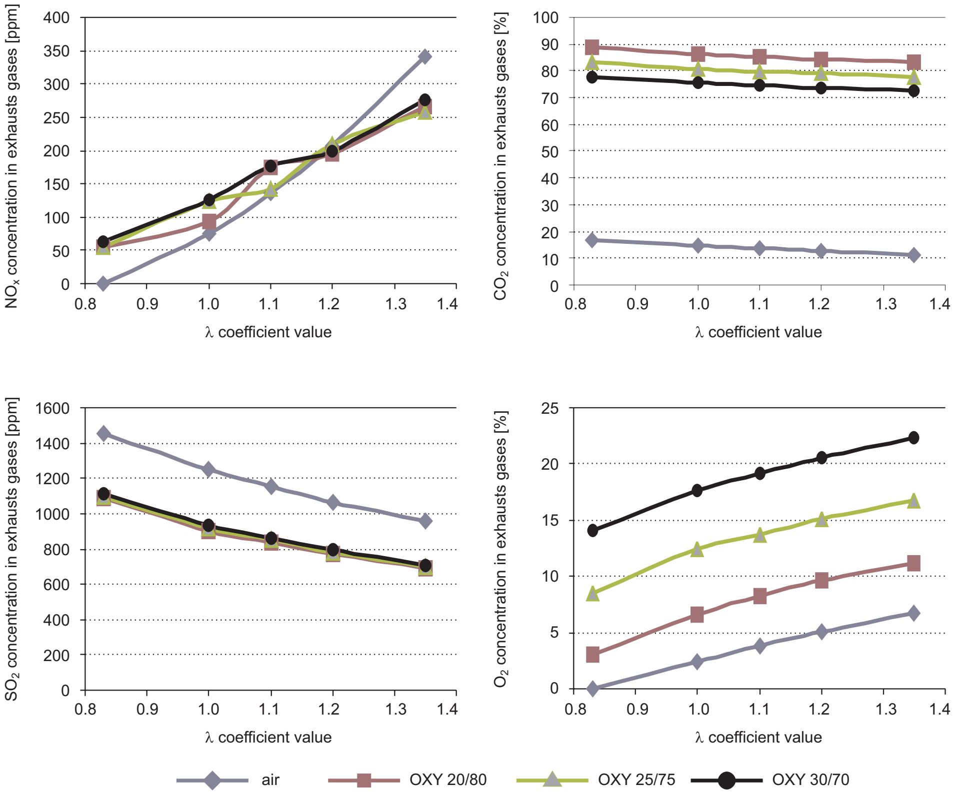

Fig. 1. The concentration of NO_x, SO_2, O_2 and CO_2 in lambda coefficient function for various OXY atmosphere (7 % humidity content in the fumes) during pulverized hard coal combustion

The nitric oxides concentration was rapidly rising due to lambda coefficient increase – in case of all oxy-coal combustion processes a concentration range was reduced and its maximum level is lower more than 100 ppm in comparison to air combustion.

Despite the fact that SO_2 concentration pattern is similar for all oxy-atmospheres and for the air-atmosphere, the SO_2 contents in the exhausts in case of oxy-coal combustion is about 400 ppm lower in comparison to air-combustion process.

Simulation of brow coal combustion process

In Table 3 the simulation results for brown coal are presented for each lambda value and humidity function.

In Fig. 2 the chosen results of particular exhaust gases components concentrations are presented in lambda coefficient function on example of 7 % humidity content in the fumes.

Similarly to hard coal, the highest carbon dioxide concentration was observed during the fuel combustion in 20/80 oxy-atmosphere, the insignificant decrease of CO_2 concentration was noticed for other oxy-coal combustion processes (the oxygen share

Table 3

Simulation results for pulverized brown coal combustion: NO_x, SO_2, CO_2, O_2 concentrations in λ and humidity function

	NO_x [ppm]				SO_2 [ppm]				CO_2 [% vol.]				O_2 [% vol.]			
φ %	0	7	14	21	0	7	14	21	0	7	14	21	0	7	14	21
λ	air															
0.83	230	338	395	491	378	361	340	319	15.5	14.6	13.7	12.7	1.6	2.4	3.4	4.3
1.00	397	444	582	608	320	305	287	270	13	12.3	11.5	10.8	4.6	5.3	6.1	6.8
1.10	479	503	656	855	296	282	265	249	12	11.3	10.6	9.9	5.8	6.5	7.22	7.9
1.20	599	617	731	814	274	261	245	230	11.1	10.4	9.8	9.2	7	7.6	8.2	8.9
1.35	747	708	828	845	244	233	220	206	9.9	9.4	8.8	8.3	8.4	8.9	9.5	10.1
λ	OXY 20/80															
0.83	213	305	336	372	277	263	247	233	85	83.6	82.3	80.8	5.7	6.6	7.5	8.4
1.00	357	390	470	510	233	221	208	195	83.3	82.2	81	79.8	8.9	9.6	10.4	11.1
1.10	406	458	497	644	215	204	192	180	82.6	81.6	80.5	79.4	10.2	10.8	11.5	12.3
1.20	479	510	602	677	198	188	177	166	81.9	81	80	79	11.4	11.9	12.6	13.3
1.35	569	616	774	834	178	168	159	149	81.2	80.3	79.4	78.6	12.9	13.4	13.9	14.5
λ	OXY 25/75															
0.83	217	301	352	399	282	267	252	236	79.5	78.2	76.8	75.5	11.1	12.1	12.9	13.8
1.00	327	395	423	538	237	225	212	199	77.8	76.7	75.5	74.4	14.4	15.1	15.8	16.5
1.10	400	467	587	622	218	207	196	183	77.1	76.1	75	74	15.7	16.4	17	17.7
1.20	434	535	545	707	201	191	180	169	76.4	75.5	74.5	73.6	16.9	17.5	18.1	18.7
1.35	570	742	735	864	180	171	161	151	75.6	74.8	73.9	73	18.4	18.9	19.5	20
λ	OXY 30/70															
0.83	240	273	307	452	287	272	256	239	74.2	73	71.7	70.3	16.4	17.2	18.1	19
1.00	340	404	465	584	241	228	215	201	72.5	71.4	70.3	69.2	19.7	20.4	21.1	21.7
1.10	396	423	541	581	222	210	199	186	71.7	70.7	69.7	68.7	21.1	21.7	22.3	22.9
1.20	468	540	628	690	204	194	183	172	71	70.2	69.2	68.3	22.3	22.9	23.4	24
1.35	540	660	788	787	183	173	164	153	70.2	69.4	68.6	67.7	23.8	24.4	24.8	25.4

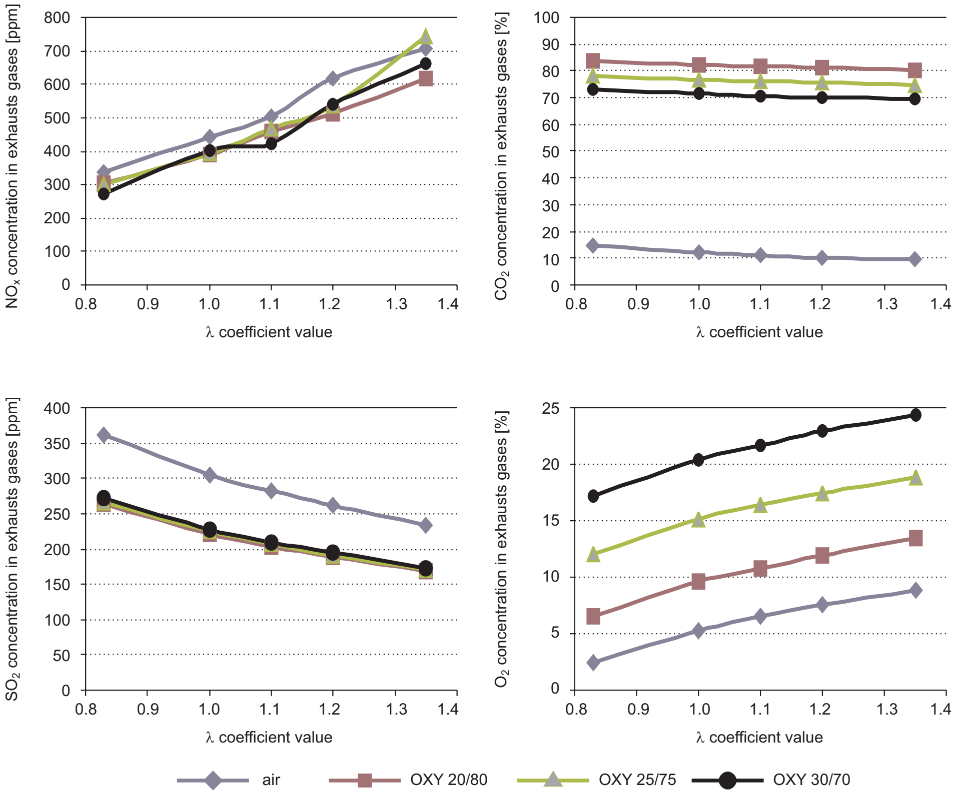

Fig. 2. The concentration of NO_x, SO_2, O_2 and CO_2 in lambda coefficient function for various OXY atmosphere (7 % humidity content in the fumes) during pulverized brown coal combustion

increase in OXY-combustion caused CO_2 concentration reduction). In case of brown coal combustion CO_2 concentrations are approximately 10 % lower than for hard coal in all atmospheres.

The nitric oxides emission in process of brown coal combustion is significantly higher than for hard coal (concentration range: near zero to 350 almost ppm for hard coal and 270 to 740 for brown coal). The highest value of NO concentration was noticed for 27/75 OXY combustion (for air combustion – in hard coal combustion process).

The lower sulfur content in the fuel caused also 4 times lower SO_2 concentration in comparison with hard coal. For all OXY-atmospheres the concentrations in function of lambda coefficient is almost 100 ppm higher than in case of air-combustion (similar situation was observed for hard coal combustion)

Summary

CFD approaches have been used in studies to better understand the flowfield and combustion processes in oxy-coal combustion and provide predictions of minor species and pollutant formations. Radiation heat transfer plays a major role in the furnace, and it also governs the energy equation in combustion. The authors of the paper applied turbulence-radiation model for simulation.

The results of the modeling oxy-coal combustion indicate that the method is more advantageous in aspect of pollutant emission than air-combustion of coal. The fuel comparison analysis indicates that for brown coal combustion lower CO_2 but higher NO and SO_2 emission was observed than for hard coal. The pollution formation in the reactor seems to proceed in visible different mode than in air-coal combustion process. The CFD modeling of the oxy-coal combustion process is a proper tool for oxy-coal process investigation and understanding for better control of pollutant emission by combustion parameters optimization.

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ZASTOSOWANIE NUMERYCZNEJ MECHANIKI PŁYNÓW W MODELOWANIU SPALANIA WĘGLA W ATMOSFERZE POWIETRZA I OXY

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Abstrakt: Pomimo faktu gwałtownego rozwoju sektora alternatywnych źródeł energii w ostatnich dziesięcioleciach, spalanie węgla jako najważniejszego źródła energii konwencjonalnej (w szczególności w Polsce) jest bardzo istotnym zagadnieniem w aspekcie ochrony i inżynierii środowiska. Nowe wyzwania w zakresie obniżania emisji związków toksycznych, a także gazów cieplarnianych wymuszają rozwój w zakresie innowacyjnych technologii spalania węgla: pierwotnych (na etapie substratów) oraz wtórnych (na etapie produktów), a także modyfikacji procesu spalania (atmosfera OXY). W artykule zajęto się zagadnieniem formowania się zanieczyszczeń (NO_x oraz SO_2) powstających podczas procesu spalania pyłu węgla kamiennego i brunatnego w atmosferze powietrza oraz atmosferze OXY.

Do obliczeń CFD przepływu i spalania mieszanki powietrzno-węglowej wykorzystano model laboratoryjnego pieca opadowego. Jako warunki materiałowe do obliczeń posłużono się rzeczywistymi analizami techniczno-elementarnymi pyłu węglowego. Przedziały frakcyjne cząstek ustalono na podstawie analizy sitowej. Warunki brzegowe (temperaturę pieca, doprowadzanego powietrza oraz paliwa, natężenia przepływu powietrza pierwotnego i wtórnego) ustalono na podstawie pomiarów rzeczywistych w warunkach laboratoryjnych. W celu zamodelowania spalania z uwzględnieniem radiacji wykorzystano model WSGGM (weighted – sum – of – gray – gases model). Obliczenia z uwzględnieniem radiacji oraz powstawania zanieczyszczeń NO_x i SO_2 prowadzono dla warunków spalania w powietrzu oraz przyjęto różnicowane atmosfery OXY. Obliczenia prowadzono w funkcji wartości współczynnika lambda oraz dla różnych wartości wilgotności paliwa.

Słowa kluczowe: modelowanie CFD, spalanie pyłu węglowego, węgiel kamienny, węgiel brunatny, OXY, radiacyjny model spalania

DOI: 10.2428/ecea.2013.20(04)043 ECOL CHEM ENG A. 2013;20(4-5):461-468

Maciej ZAWIŚLAK[1]

IMPACT OF VEHICLE INTERIOR GEOMETHRY MODIFICATIONS ON CARCINOGENS DISTRIBUTION IN CABIN ATMOSPHERE

WPŁYW MODYFIKACJI GEOMETRII KABINY POJAZDU NA ROZKŁAD ZWIĄZKÓW RAKOTWÓRCZYCH W ATMOSFERZE WNĘTRZA

Abstract: The phenomena of volatile carcinogens pollution of interior atmosphere is an important issue on public health field. A car vehicle is a specific environment of human life where levels of volatile compounds concentration are much more higher than *ie* in buildings (houses or offices). Statistic research on Wroclaw citizen group prove that most car-users suffer from inconvenience caused by specific, plastic-base, scents inside car cabin caused by different groups of volatile organic compounds (VOCs).

The VOCs sources can be divided on external (polluted air inlet through vehicle ventilation system) an internal (emission from cabin equipment materials). The volatile organic compounds are absorbed by human body mostly by respiratory system. The significant impact on toxicological characteristic of in-vehicle VOCs, in parallel with physical-chemical properties of the substance and exposition time, has also concentration distribution in vehicle cabin, especially the concentration on user head level.

In the paper the results of CFD simulation of cabin geometry impact on chosen VOCs (benzene and toluene) distribution is presented. The geometrical model of vehicle cabin has been made and its insignificant modification was conducted to proof cabin geometry impact on driver exposure on the carcinogens carried out by ventilation system.

Keywords: CFD modeling, vehicle interior, volatile organic compounds

Introduction

Many organic compounds are known to cause cancer in animals; some are suspected of causing, or are known to cause, cancer in humans [1]. From volatile organic compounds group especially BTX (benzene-toluene-xylene and their isomers) have been classified as a human carcinogens by IARC (1982) and was listed by both

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the European Commission and the World Health Organization as one of the top-priority compounds for the development of guidelines for indoor air quality (EC JRC, 2005; WHO, 2006). As with other pollutants, the extent and nature of the health effect will depend on many factors including the level of exposure and length of time exposed.

Statistic research on Wroclaw citizen group prove that most car-users suffer from inconvenient caused by specific, plastic-base, scents inside car cabin caused by different groups of volatile organic compounds (VOCs) (Fig. 1).

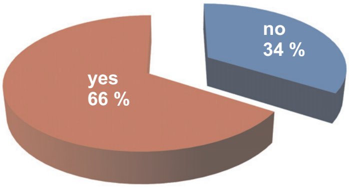


Fig. 1. Respondents answer for a question: Have you ever felt inconvenience caused by specific smell inside car cabin? (Own statistic research based on Wroclaw citizens)

Most of the respondents feel plastic-based, synthetic odors or fuel/organic solution mixtures (Fig. 2).

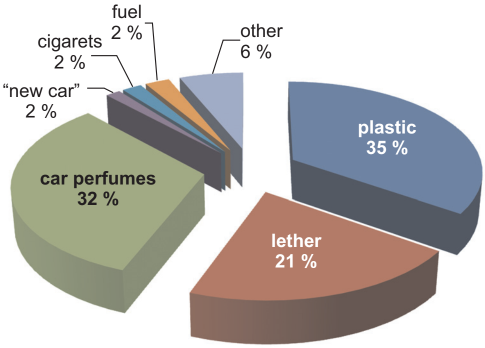


Fig. 2. Car cabin scents noticed by car users (own statistic research based on Wroclaw citizens)

Compounds responsible for this kind of scents are generally high-toxic volatile aromatic hydrocarbons represented by benzene.

Benzene concentrations measured in vehicles are generally higher than those outdoors. Levels of benzene measured in vehicles in Europe ranged from 13 to 42 μg/m^3, while lower levels of 1.3–3.8 μg/m^3 were measured in a recent United Kingdom study [2]. Benzene levels measured in Mexico and the United States ranged from 1.7 to 42 μg/m^3 and a similar range (0.5–47 μg/m^3) was found in several Asian cities [3]. The highest in-vehicle benzene levels were measured in Italy in the early 2000s, with geometric means ranging from 17 to 101 μg/m^3 [3].

The aim of this study was CFD simulation of cabin geometry impact on chosen VOCs (benzene, toluene and xylene) distribution is presented. The geometrical model of vehicle cabin has been made and its insignificant modification was conducted to proof cabin geometry impact on driver exposure on the carcinogens carried out by ventilation system.

Methodology

As an object for modeling chosen aromatic compounds particle distribution geometry passenger-vehicle (Fiat Grande Punto) was chosen as an examples of basic geometry of popular car vehicle. Three-dimensional computational model of sampler was design in Gambit software (Fig. 3).

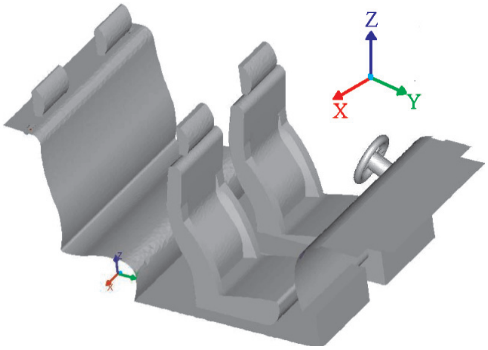


Fig. 3. Grande Punto geometry model (Gambit software)

For flow modeling application FLUENT-ANSYS software was applied. Numerical mesh on tetra elements was made. Two-equational k-ε turbulence model was applied. For particle of chosen VOCs modeling DPM model was used.

For simulations boundary conditions of benzene and toluene was based on chromatographic analysis on real object (Emission Research Laboratory, Varian 450GC-FID chromatograph) in a brand new passenger. The VOCs samples was up-taking in points set according to ISO/DIS 12219-1draft [4].The temperature and pressure was kept in standard conditions of human existence (293 K, 101300 Pa).

The vehicle geometry was modified as in Table 1.

Table 1

Geometry modifications variants

Symbol	Geometry variant	Dimension		
		Width	Length	Height
B	Basic geometry	X	Y	Z
E1	Resized geometry (expanded): variant 1	X + 10 %	Y	Z
E2	Resized geometry (expanded): variant 2	X	Y + 10 %	Z
E3	Resized geometry (expanded): variant 3	X	Y	Z + 10 %

Boundary conditions

In Table 2 boundary conditions for simulation are presented:

Table 2

Boundary conditions for modeling

Compounds concentration [kg/m^3]	
Benzene (and isomers)	$1.58 \cdot 10^{-6}$
Toluene (and isomers)	$3.14 \cdot 10^{-6}$
Flow set	
Flow intensity [m^3/s]	$4.2 \cdot 10^{-4}$ m^3/s
Ventilation system mode	Central ventilation nozzles

Results

The results was presented in tables and figures below.

In Fig. 4 the air stream lines are presented according to applied ventilation system set (Table 2).

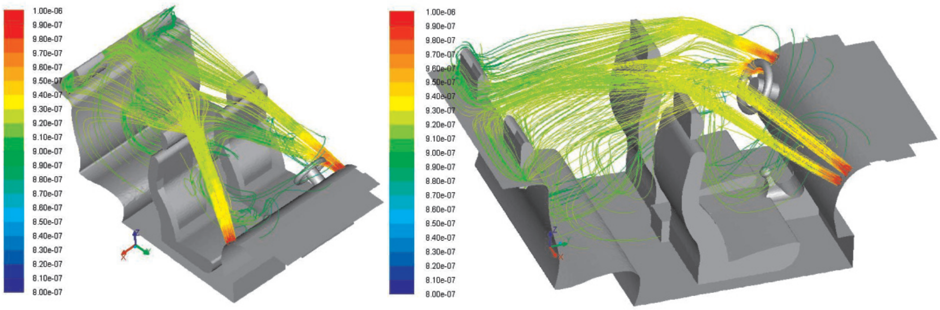


Fig. 4. Flow intensity stream lines, m3/s (central nozzles mode)

In Table 3 the results of modeling – benzene and toluene concentration distributions in analyzed variants of geometry models are presented for all Y-Z cross-sections.

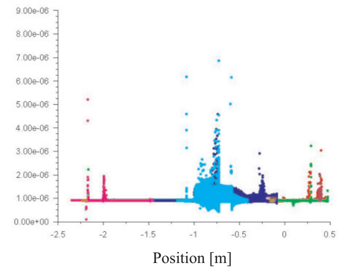
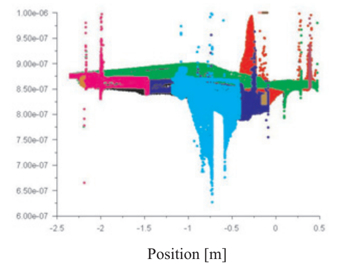
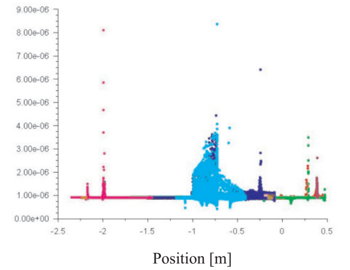
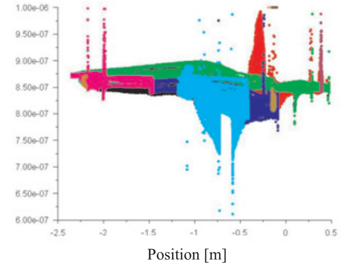
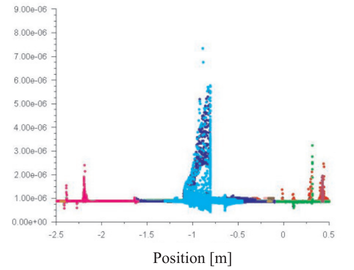
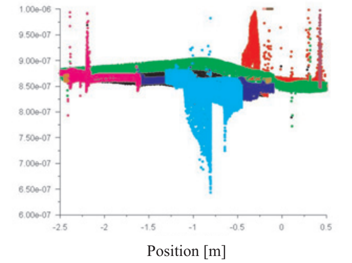
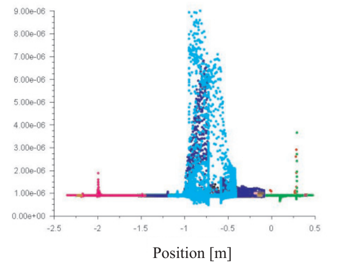
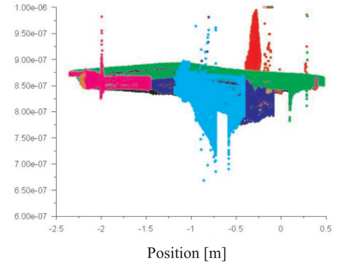
According to the modeling results it is visible that even insignificant (10 % in one dimension) changes in vehicle geometry cause change in carcinogens distribution, especially for particular health-hazardous benzene.

For driver exposure investigation, as a most exposed vehicle user because of in-vehicle time residence, the cross-section on driver position (Fig. 5) was separately analyzed.

The results of the simulation on a cross-section on driver position are presented in Table 4.

Table 3

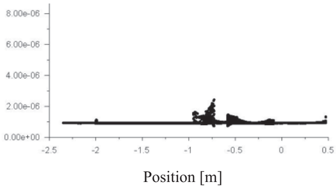
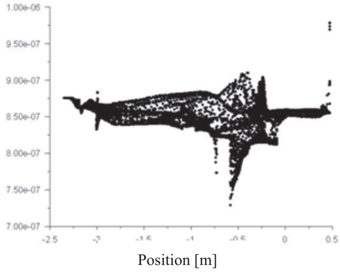
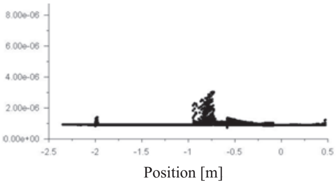
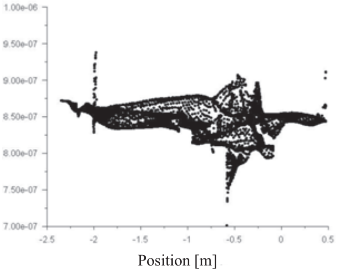
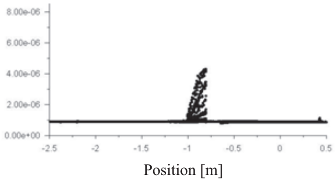
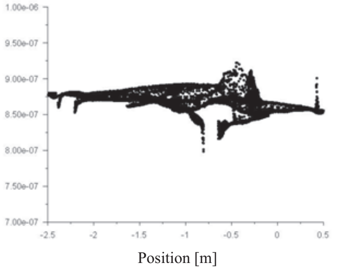
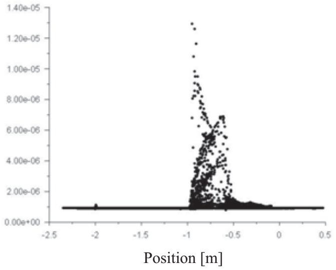
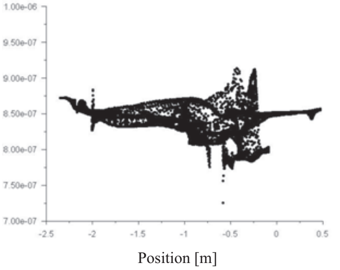
Benzene and toluene volume fraction distribution on all Y-Z cross-sections

Volume fraction	
Benzene	Toluene
B	
	
E1	
	
E2	
	
E3	
	

- ● sidewall
- ● cocpit
- ● topwall
- ● florwall
- ● frontseat
- ● backseat
- ● inlet: driver-bottom
- ● inlet: driver-top
- ● inlet: passenger-bottom
- ● inlet: passenger-top
- ● inlet: central
- ● inlet: front window
- ● outlets

Table 4

Benzene and toluene volume fraction distribution on driver position (according Fig. 3)

Volume fraction	
Benzene	Toluene
B	
	
E1	
	
E2	
	
E3	
	

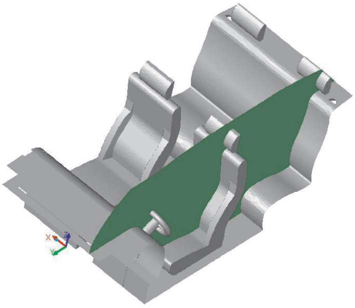


Fig. 5. Cross-section on driver position

The highest benzene concentrations on driver position (fronseat) was observed in case E3 geometry variant (10 % interior height expand) . The basic variant seems to be most advantageous for benzene distribution. Analyzing toluene dispersal the most advantageous is E2 variant (10 % extend of vehicle length). For both volatile compounds the impact of geometry change on carcinogens distribution is visible.

Summary

To discuss the toxicological characteristic of in-vehicle VOCs, in parallel with physical-chemical properties of the substance and exposition time, also carcinogens concentration distribution in vehicle cabin, especially the concentration on user head level need to be consider. CFD modeling enable in a relative short time analyze different geometry variants of vehicle interior and evaluate their impact on volatile individuals distributions.

The paper presents results of the modeling of benzene and toluene distribution inside popular passenger car and the impact of insignificant interior geometry modifications on those compound concentration. According to the simulations some conclusions should be emphasized:

– The analyzed geometry variations impact on benzene and toluene concentrations.

– The most advantageous variant in aspect of driver exposure seems to be basic variant (B) for benzene and 10 % length expand variant (E2) for toluene.

– The results of the modeling indicate on its applicability to evaluate the vehicle user exposure on particular volatile carcinogens. The researches need to be expanded on more geometry modifications (also geometry reduction and mixed variants) for finding optimal variant of particular vehicle interior in aspect of human health exposure on VOCs carcinogens.

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WPŁYW MODYFIKACJI GEOMETRII KABINY POJAZDU NA ROZKŁAD ZWIĄZKÓW RAKOTWÓRCZYCH W ATMOSFERZE WNĘTRZA

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Abstrakt: Obecność kancerogenów z grupy lotnych połączeń organicznych, w szczególności w pomieszczeniach zamkniętych jest istotnym problemem z zakresu zagadnień w obszarze zdrowia publicznego. Pojazd samochodowy jest środowiskiem życia człowieka, w którym poziomy stężeń substancji z grupy lotnych połączeń organicznych znacznie przekraczają stężenia w budynkach mieszkalnych czy biurowcach. Źródła LZO w kabinie pojazdu można podzielić na dwa rodzaje: zewnętrzne (zanieczyszczone powietrze wprowadzane do wnętrza kabiny za pomocą systemu wentylacyjnego pojazdu) oraz wewnętrzne (emisja z materiałów stosowanych we wnętrzu kabiny pojazdu). Lotne związki organiczne przedostają się do organizmu ludzkiego głównie za pomocą dróg oddechowych, a na ocenę ich wpływu toksycznego na zdrowie użytkowników oprócz właściwości fizykochemicznych substancji oraz czasu ekspozycji ma również znaczący wpływ dystrybucja tych substancji we wnętrzu pojazdu, a w szczególności ich koncentracja na wysokości głowy użytkownika.

W niniejszym artykule zaprezentowano wyniki symulacji komputerowej (metoda CFD) cyrkulacji powietrza wewnątrz kabiny pojazdu w aspekcie rozkładu wybranych kancerogenów z grupy LZO (benzenu i toluenu). Wykonano model geometryczny kabiny pojazdu, a następnie poprzez nieznaczne modyfikacje geometrii wnętrza udowodniono wpływ geometrii na narażenie kierowcy na kontakt z lotnymi substancjami o charakterze kancerogennym wprowadzanymi poprzez system wentylacyjny pojazdu.

Słowa kluczowe: modelowanie przepływów, wnętrze pojazdu, lotne związki organiczne

DOI: 10.2428/ecea.2013.20(04)044 ECOL CHEM ENG A. 2013;20(4-5):469-480

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and Marcin ZIELIŃSKI[1]

ODOUR NUISANCE ACCOMPANYING HYPOLIMNETIC WITHDRAWAL METOD ON THE EXAMPLE OF THE KORTOWSKIE LAKE

UCIĄŻLIWOŚĆ ZAPACHOWA PRZY SELEKTYWNYM USUWANIU WÓD HYPOLIMNIONU NA PRZYKŁADZIE „EKSPERYMENTU KORTOWSKIEGO”

Abstract: The aim of this study was to determine the odour nuisance accompanying the restoration of Kortowskie Lake. The measurements of odour concentrations have been conducted during the summer season of 2012. Odorous gas samples were taken during the removal of hypolimnion water. Along the test section located Kotowki six sampling points. Odour concentration value at the designated measuring points were determined by dynamic olfactometry yes/no method. The study was performed in accordance with PN-EN 13725 by using the olfactometer TO8.

Keywords: odour nuisance, *Olszewski's Pipeline*, olfaktometric measurements, European Odour unit

Introduction

Contemporarily, an increase is observed in social awareness of the significance of environment protection. Many institutions are established, at both the global and local level, the objective of which is to enact and execute law related to environment monitoring, to counteract environment degradation and to recultivate areas and ecosystems damaged by anthropogenic activity. The VIth Environment Action Programme of the European Community, adopted the following actions to be undertaken in the four priority areas for the first decade of the XXIst century:

– stopping climate changes;
– protection of nature and biodiversity;

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- sustainable use of natural resources and waste management;
- assurance of the quality of environment appropriate to human health [1].

Once evaluating this Program, the European Commission claims that it is necessary to take account of results of investigations on the impact of environment on health in policies assuming its protection. To this end, in Poland monitoring is conducted in terms of:

- air quality;
- waters quality;
- soil and earth quality;
- noise;
- wastes;
- electromagnetic fields;
- ionizing radiation.

However, no consideration was given to odour nuisance so far. Problems of odourants emission are not regulated by executive authorities, owing to a lack of executive regulations to respective laws [2, 3].

Odour nuisance is one of the symptoms of the negative effect of pollutions on the natural environment and surrounding of man. It is a discomfort evoked by substances or circumstances accompanying them, that may negatively affect a single person or a group of people by inducing poor physical and mental state, and sometimes even a loss of health [4, 5]. Within programs of health protection and environment protection, the legislative bodies of highly-developed countries tackle a problem of regulating admissible levels of emissions of odour pollutants. In Germany, France, the Netherlands, Great Britain, Japan, the USA, and Canada standards have been elaborated that are binding in the industry and agriculture, as well as other branches of economy [6].

Dynamic olfactometry

The perception of odours as unpleasant and their nuisance depend, most of all, on individual characteristics of man, *eg* aroma preferences or temper. Of significance are also extrinsic factors, an appropriate combination of which may either debilitate or strengthen the sensation of discomfort as a result of perceived odour, *eg* ambient temperature, level of noise, and duration of exposure. The determination of cause-and-effect correlations between emission of odourants and the occurrence of odour nuisance is impossible with conventional physicochemical methods. The quantification of odour – being a sensual impression – is hardly possible. For this reason, the only appropriate solution enabling odour nuisance assessment seems to be the application of a human nose as an analyzer. The objective quantification of the concentration of an odourant is a task of olfactometry. Its objective is to determine detection threshold, namely the boundary moment of olfactory sensitivity. The olfactometric analysis results in the expression of an olfactory sensation in arbitrary measuring units [4–7].

Following the example of countries that had implemented international standards, Poland has its own standard PN-EN 13725:2007 that stipulates principles of determining odour concentration by dynamic olfactometry. This standard is an exact translation of the European Standard EN 13725, approved by the Polish Committee for Standardization (PKN).

Three types of olfactometric analysis may be distinguished:

– analysis of odour concentration;

– analysis of odour intensity;

– analysis of hedonistic effect.

Olfactometric analysis is conducted by persons characterized by high olfactory sensitivity. Each odour panel is formed on the base of meticulous selection. The olfactory sensitivity is verified by means of standard material, being *n*-butanol. The geometric mean of 10–20 measurements individual detection threshold for a reference material – *n*-butanol ($ITE_{n\text{-}butanol}$) ought to fit within the range of 62–246 μg/m^3. The antilogarithm from standard deviation of the assessment of individual threshold of *n*-butanol (s_{ITE}) should be lower than 2.3. The olfactory efficiency of panelists should be regularly controlled and verified in terms of compliance with selection criteria. Consistency to those requirements enables achieving objective, repeatable and reproducible experimental results [8].

Based on achieved results of measurements, odour concentration is computed at particular points of odour emitters environment. The knowledge of production profile, extent of emission, landform features, and meteorological conditions affords the possibility of modeling and predicting odours dissemination. It is especially significant in the case of emitters located in centers of social agglomeration or in its close vicinity. This has been emphasized in the VIth Environment Action Programme of the European Community, where account was taken of the improved status of urban environment in all policies, for as many as 75 % of the EU populations live in cities. An interesting example, in this respect, is the selective removal of hypolimnion waters enabling recultivation of the Kortowskie Lake. It is a pro-environmental action, yet characterized by excessive odour nuisance, realized in the centre of the most beautiful campus in Poland at the University of Warmia and Mazury in Olsztyn.

The Kortowski Experiment

The Kortowskie Lake is located in the south-western part of the city of Olsztyn, on the area of Kortowo – the campus of the University of Warmia and Mazury in Olsztyn. In the 1950-ies, waters of this lake were heavily contaminated and the aquifer exhibited a strong eutrophic character. This condition was caused by irresponsible wastewater management and the contemporary agricultural policy. During winter and spring stagnation, a lack of oxygen dissolved in water was observed as early as at the depth of 5 m. In addition, a high level of hydrogen sulfide was noted in the waters. Intensive phytoplankton blooms occurred from April till September [9]. In order to save the lake, a pioneering attempt has been undertaken on the initiative of Prof. Przemysław Olszewski that involved technical recultivation of the lake with the method of selective removal of waters from hypolimnion. Accordingly to method assumptions, the removal of eutrophicated and anoxic waters from hypolimnion outside of lake ecosystem should lead to the inhibition of rapidly proceeding degradation processes. The long-term objective of this method was to initiate the process of aquifer oligotrophication. The selection of method was dedicated by appropriate morphometric determinants of the lake basin and characteristics of catchment area [10].

At the first stage of recultivation (1956–1974) a wooden tube was built, the inlet of which was placed on the bottom of the Southern Lake Basin. Owing to water lifting, hydrostatic pressure was achieved in the lake that was enforcing spontaneous flow of water in the pipeline. The anoxic and contaminated with biogenes waters of hypolimnion were discharged to a small river, called Kortowka, flowing through the lake (Fig. 1).

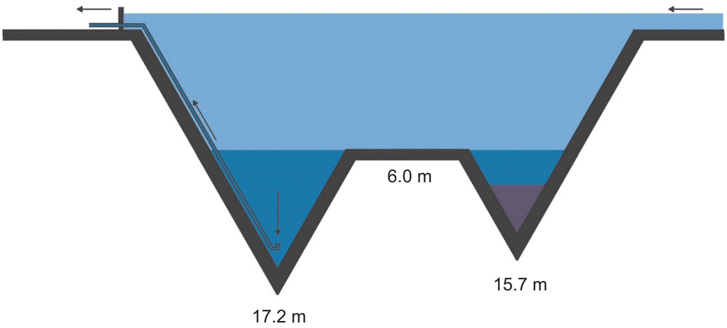

Fig. 1. Scheme of the Kortowski Experiment

Effects of the first stage of recultivation included:
- increased thickness of oxygenated water strata;
- elimination of hydrogen sulfide;
- reduced quantity of phytoplankton;
- shortened period of oxygen deficits;
- acceleration of autumn circulation;
- removal of a significant quantity of biogenic substances – total phosphorus (by 158 % compared to the inflowing load), and total nitrogen (by 28 %) [11–14].

In the year 1976, the exploited wooden pipeline was replaced by a tube made of glass fiber and polyester resins. In such a form, the pipeline is functioning to this day. Its length is 250 m, its diameter is 600 mm, and the maximum flow rate reaches 0.25 m^3/s. At the maximum efficiency of water flow in the pipeline, the positive changes were maintaining till the end of 1989 when the lake reached the state of moderate eutrophy. Effects of the second stage of the Kortowskie Lake recultivation are no longer so spectacular. The current improvement is determined by the hydrological balance, to be more specific – by the volume of water inflowing to the lake. The necessity of maintaining the water regime does not allow the pipeline to work with the maximum efficiency in the period of summer stagnation. Unfortunately, the unfavorable hydrological conditions caused that since the mid of the 1990-ies, the lake has begun to evolve into the state of advanced eutrophy [15–18].

Unfavorable effects, relatively low capital investments and null exploitation investments have made this method highly attractive compared to other, contemporarily applied solutions. The long-term recultivation of the Kortowskie Lake with the *Olszewski's Method* has contributed to a significant improvement of waters quality and prevented the complete degradation of the aquifer. Nevertheless, discharging waters of hypolimnion with sedimenting organic matter to the Kortowka river caused that unpleasant and sometimes oppressive odour was perceptible in river vicinity.

Study object

The object of the study was a fragment of the Kortowka river running through the campus of the University of Warmia and Mazury in Olsztyn, from the site where the river has its source in the Kortowskie Lake (outlet of *Olszewski's Pipeline*) to Warszawska Street. The length of this fragment, measured alongside the river-bed, is 625 m. The river valley is U-shaped. Banks of the initial 70-m fragment are low – ca 0.5. In the other part of the analyzed fragment of the Kortowka river, the banks are relatively high – ca 2.4 m. Alongside the river, except for the 107-m central fragment, trees and dense gramineous vegetation are overgrowing the banks. The middle fragment is overgrown exclusively with grass. At the whole examined length, the river is not more than 2 m wide. It is very shallow, and its depth reaches ca 0.3 m. An exception is the mouth of the Kortowskie Lake with the outlet of the *Olszewski's Pipeline*. At a water dam, the depth reaches ca 2 m. River current at this fragment is slow and quiet. From the south, the river valley is enclosed by an elevation (Gorka Kortowska (mountain) – 128.6 above sea level) (Fig. 2).

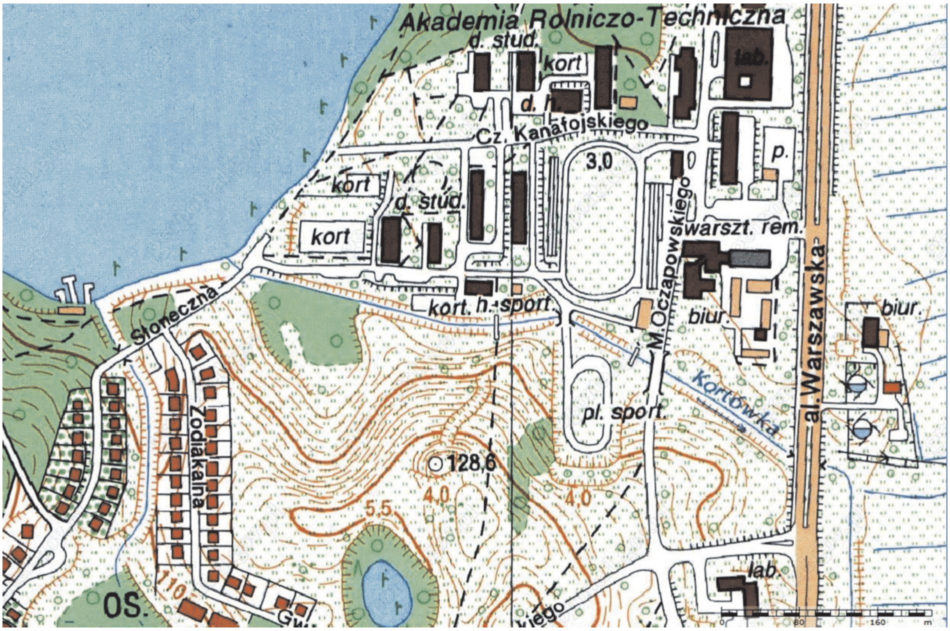

Fig. 2. Topographic map of area around the Kortowka river [19]

Methods

The odour nuisance of the *Kortowski Experiment* was investigated since the 3rd of July till the 21st of August 2012. Continuous, selective discharge of hypolimnion waters produced during winter stagnation occurred in this period. Six sampling sites were located alongside the analyzed fragment of the Kortowka river:

1 – river outlet from the Kortowskie Lake;
2 – bridge at the dormitory (DS, 150 away from the outlet from the lake);
3 – bridge at the gym (280 m);
4 – bridge at the stadium (350 m);
5 – bridge at the library (460 m);
6 – bridge at the Center of Aquaculture and Environment Engineering (625 m) (Fig. 3).

Fig. 3. Location of sampling sites [19]

All sampling sites constituted a surface source of odourants emission. Odouriferous gases were collected using a STANDARD sampler to foil bags NELOPHAN, that had been earlier conditioned. The sampler by ECOMA company was equipped in a cover with air blow and floats enabling sample collection from a liquid surface. After collection, the material was immediately transported to a stationary olfactometric laboratory at the Department of Environment Engineering (no. 7 on the map). The time span between sample collection and determination of odour concentration was not longer than 1 h. Dynamic dilutions were applied accordingly to the Polish Standard PN-EN 13725: "Air quality. Determination of odour concentration with dynamic olfactometry". Analyses were carried out with a TO8 four-station automatic olfactometer by ECOMA. Determination of odour concentration was conducted with the yes/no method. During measurements, temperature and concentration of CO_2 were monitored in the room. Analyses were carried out by two four-person panels and an operator.

The operator was providing a series of decreasing dilutions of sample (Z) with the factor of step $F_s = 2$ to each panel. The measuring range of the olfactometer, without initial dilution of the sample, ranged from $Z_{\min} = 2^2$ to $Z_{\max} = 2^{16}$. The initial dilution was adjusted so as to enable detecting odour presence already after presentation of the third step. Each of the series contained 20 % of blank samples with pure, odourless air that were presented to panelists at random. One measurement consistent of one warm-up series and three measuring series. The value of an individual detection threshold of a series of dilutions (Z_{ITE}) was computed as a geometric mean of the last "I do not smell" (Z_{NO}) and the first of the two successive "I smell" (Z_{YES}). In order to achieve the panel detection threshold ($\overline{Z}_{ITE,\,pan}$), geometric mean was computed from all individual detection thresholds ($\overline{Z}_{ITE}$). Next, reverse screening of the panelists was conducted by calculating the screening parameter (ΔZ) according to the following formula:

$$- \text{ if } Z_{ITE} \geq \overline{Z}_{ITE} \rightarrow \Delta Z = \frac{\overline{Z}_{ITE}}{Z_{ITE}},$$

$$- \text{ if } Z_{ITE} \leq \overline{Z}_{ITE} \rightarrow \Delta Z = -\frac{Z_{ITE}}{\overline{Z}_{ITE}}.$$

Results of measurements exceeding the range of $-5 \leq \Delta Z \leq 5$ were not considered. The value of odour concentration was expressed in European Odour units per cubic meter [ou_E/m^3] following the formula: $c_{od} = \overline{Z}_{ITE} \times 1\ ou_E/m^3$. The geometric mean from three group detection thresholds ($\overline{Z}_{ITE,\,pan}$) was adopted as the final odour concentration.

Presentation of results

Final results of measurements of odour concentration (c_{od}) were presented in Table 1. Results achieved in the study will allow to plot the course of odour concentration variability alongside river reaches.

In six out of the eleven cases, the highest odour concentration was noted at the first measuring site – at the *Olszewski's Pipeline* outlet. At the successive bridges, the concentration was observed to decrease exponentially along with the increasing distance from that site (Fig. 4).

The highest determined concentration of odourants reached 34218 ou_E/m^3 and was noted on the 3rd of August 2012. On the 6th of July and the 22nd of August 2012, at the sixth measuring site, the odour concentration was undeterminable.

Table 1

Final values of odour concentration measurements

Research position number	Date of sampling											Geometric mean
	05.07.2012	06.07.2012	30.07.2012	31.07.2012	03.08.2012	10.08.2012	20.08.2012	21.08.2012	22.08.2012	23.08.2012	24.08.2012	
	Odor concentration value c_{od} [ou_E/m^3]											
1	609	2391	431	6596	34218	724	5161	91	3024	305	939	1404
2	861	268	490	2896	1625	318	1933	790	1149	395	362	750
3	267	108	683	469	558	542	621	636	813	204	395	420
4	1449	69	451	609	767	1218	342	305	203	99	332	370
5	748	32	54	490	1448	96	216	99	225	27	174	162
6	186	0	0	1328	684	0	813	0	0	0	256	17*

* In order to calculate the geometric mean of measurements on the research position number 6, value of 0 was replaced by value 1, it allows to calculate the mean odor concentration.

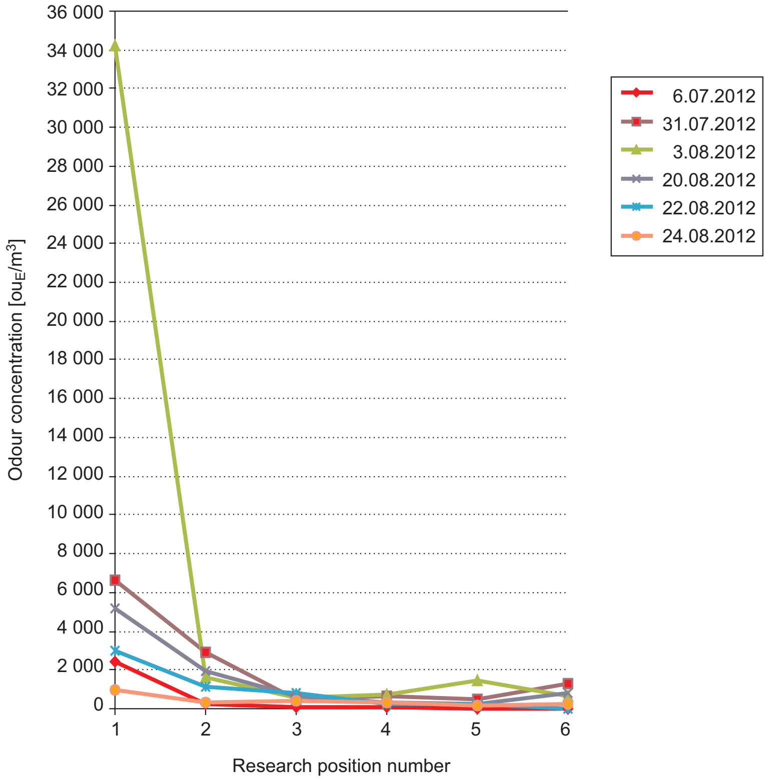

Fig. 4. The course of odour concentration variability alongside river reaches – exponential correlation

On the five other days, irregular fluctuations were recorder in odour concentration (Fig. 5).

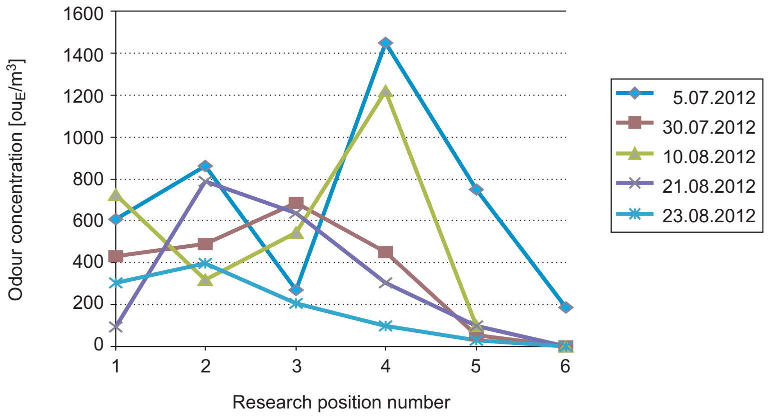

Fig. 5. The course of odour concentration variability alongside river reaches – fluctuations

Twice (on the 21st and 23rd of August 2012), the maximum concentration of odourants was assayed at the second measuring site. It accounted for, respectively: 91 and 305 ou_E/m^3. On the 30th of July 2012, the highest odour nuisance, recorded at the third measuring site, reached 683 ou_E/m^3. The maximum concentration of volatile odours on the fourth bridge was noted on the 5th of July and 10th of August 2012 (respectively: 609 ou_E/m^3 and 724 ou_E/m^3). Four times, at the last measuring site, the odour concentration was undeterminable.

Figure 6 presents the course of geometric means of all measurements at the successive measuring sites.

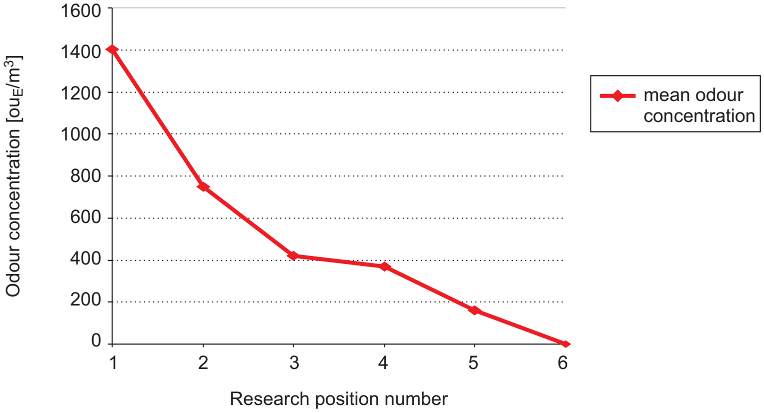

Fig. 6. The course of mean odour concentration at the successive measuring sites

As expected, the odour nuisance was decreasing along with the distance from the river outlet from the Kortowskie Lake. It was assumed that an analogous variability of odour concentration would occur on each day of measurements. This was, however, not confirmed by experimental data. For this reason, the data were subjected to a statistical analysis using STATISTICA software. The analysis did not demonstrate any correlations between study results and atmospheric conditions (temperature, pressure, humidity, wind velocity and direction).

Summary

Assuring odour comfort to populations inhabiting areas affected by odour emission requires measurements of perceptible odours. The constant monitoring of air odour enables immediate reaction to and counteracting the nuisance resulting from the appearance of odours.

In Poland, an attempt was undertaken to classify the most uncomfortable odour emitters [13], in addition odour nuisance of industrial, agricultural and municipal plants was monitored as well [17, 18].

The objective of this research was to determine the odour nuisance accompanying the selective removal of hypolimnion waters from the Kortowskie Lake. The odour concentration measured at selected sites of the Kortowka river reached even up to 34218 ou_E/m^3. The highest odour emission was noted at the outlet of *Olszewski's Pipeline*.

Results achieved in this study indicate, that there are many sources of odours emission not necessarily linked with the negative impact of man on the environment, but with the neutral impact or even an attempt of saving the environment. One of the examples of the positive emission of odours is the outcome of an attempt of saving the Kortowskie Lake undertaken in 1956 on the initiative of Prof. Przemysław Olszewski. The study object, described in this manuscript, deserves special attention, for owing to lake location, its odour nuisance affects a large population. The problem is severe, since the reduction of nuisance or application of deodourization methods are difficult. This object requires continuous monitoring and further investigations.

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UCIĄŻLIWOŚĆ ZAPACHOWA PRZY SELEKTYWNYM USUWANIU WÓD HYPOLIMNIONU NA PRZYKŁADZIE „EKSPERYMENTU KORTOWSKIEGO”

Katedra Inżynierii Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

Abstrakt: Celem pracy było określenie uciążliwości zapachowej towarzyszącej rekultywacji Jeziora Kortowskiego. Pomiary stężenia zapachowego przeprowadzono w okresie letnim 2012 r. Próbki wonnych gazów zostały pobrane podczas usuwania wód hypolimnionu. Wzdłuż badanego odcinka Kotówki zlokalizowano sześć punktów pobrania próbek. Wartość stężenia zapachowego w wyznaczonych punktach pomiarowych oznaczono metodą olfaktometrii dynamicznej tak/nie. Badania wykonano zgodnie z normą PN-EN 13725 przy użyciu olfaktometru TO8.

Słowa kluczowe: uciążliwość zapachowa, rurociąg Olszewskiego, pomiary olfaktometryczne, europejska jednostka zapachowa

DOI: 10.2428/ecea.2013.20(04)045 ECOL CHEM ENG A. 2013;20(4-5):481-489

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QUALITY OF WATER RETAINED IN THE NATURAL MOUNTAIN CATCHMENT (DAM RESERVOIR WAPIENICA)

JAKOŚĆ WÓD RETENCJONOWANYCH W NATURALNEJ ZLEWNI GÓRSKIEJ (ZBIORNIK ZAPOROWY WAPIENICA)

Abstract: The study involved assessment of the quality of water in dam reservoir Wapienica. Samples were taken from September 2011 until June 2012. The reservoir is used for providing potable water to the city of Bielsko-Biala. The catchment of the reservoir is a natural mountain catchment, without internal sources of pollution. Environmental and organizational conditions determine the good quality of water in the reservoir. Water contains little amounts of suspended matter and solutes, favorable aerobic conditions and low fertility. Also, no contamination with organic substances was reported. Water retained in the reservoir has quality category A1, thus its treatment can only consist in filtration and disinfection. Analyses showed occurrence of some heavy metals (Zn, Pb and Co) in amounts exceeding levels typical of uncontaminated natural water. Increased levels of zinc and lead might result from atmospheric deposition of contaminants, whereas occurrence of cobalt might be natural. The studies show that unmanaged mountainous regions of southern Poland may be contaminated with trace elements.

Keywords: aquatic environment, dam reservoir, mountain catchment, land use, quality of water, heavy metals

Dam reservoirs are often the source of potable water for urban agglomerations [1]. Before being directed to the water mains network, however, retained water undergoes advanced treatment. This is necessary because of common contamination of surface waters, related to municipal [2], agricultural [3] or industrial [4] anthropopressure. In large catchments, influences of various types of human activities on the water environment generally occur simultaneously, which results in complex contamination of water [5, 6]. In that respect, water supply for the city of Bielsko-Biala is specific, because one of the main sources of potable water for this city is dam water Wapienica, whose catchment is a natural mountain catchment without any internal sources of contamination. The catchment is situated in the Western Carpathians, in the mesoregion

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of the Silesian Beskids [7]. The aim of the paper was to assess the quality of water retained in reservoir Wapienica. That makes it possible to discuss the condition of the environment in the Beskids in regions without direct anthropopressure.

The dam of reservoir Wapienica was built between 1928 and 1932 and it divided the upper section of the Wapienica stream valley (Fig. 1). Its concrete structure was among the first ones of that kind in Europe at that time. The dam is 310 meters long in its top and its height (from the foundation level) is 24 m. The reservoir is managed and used for the needs of the water mains network by company AQUA S.A. With the surface at 477.60 m a.s.l., which is the maximum level of water, its area is 17.5 ha and capacity 1.05 million m^3 [8]. After exceeding the level of 477.60 m a.s.l., uncontrolled discharge of water starts by means of overflow. The capacity of the reservoir does not include any anti-flood reserve storage. Water intakes are installed at 463.00 and 467.00 m a.s.l. Hence, the minimum level of water damming is 463.00 a.s.l. The amount of water taken from the reservoir is 22.000 m^3/day on average, and the flow in the stream below the dam (minimum flow) cannot be lower than 0.061 m^3/s [9].

Fig. 1. Wapienica dam reservoir (photo by A. Jaguś)

The catchment of reservoir Wapienica is a forest catchment (Fig. 1); for that reason, monitoring of the quality of water taken from the reservoir to the water treatment plant can be carried out relatively rarely, that is twice a year [8].

Methods

The research started with the studies of the area of the catchment of reservoir Wapienica. Cartographic analyses were carried out on a 1:10000 topographic map and on thematic maps. Particular components of the natural environment were analyzed. Also, conditions of human activities in the area of the catchment were analyzed basing on specialist papers. The research was verified directly in the field, by means of observations and documentation of the qualities of the environment in the catchment and forms of human activities.

The main part of the research was based on analyses of qualitative parameters of water in the reservoir. Four samples of water were taken in the period between September 2011 and June 2012. Sampling was carried out in the zone near the dam of the reservoir, in the region of water intakes. The samples were transported to the Central Laboratory of AQUA S.A., where several dozen parameters of water quality were determined (the paper will present results of selected markings only). The laboratory is accredited by the Polish Center for Accreditation. The analyses were carried out according to ISO norms as well as Polish norms.

Results and discussion

The catchment of reservoir Wapienica is located on northern slopes on the Silesian Beskids and covers the area of 11.1 km^2. It is closed by a dam situated in the upper section of the Wapienica stream (km 17 + 770). The catchment has a funnel-like shape and is situated meridionally. The divide runs along the following major peaks: Szyndzielnia (1028.3 m a.s.l.), Klimczok (1117.3 m a.s.l.), Stolow (1035.2 m a.s.l.) and Blatnia (917.0 m a.s.l.). Water downflow runs from the south to the north in the form of two streams: the Blatnia (upper course of the Wapienica) and the Barbara. The streams flow into the reservoir and are its main feeding watercourses. The catchments of the Blatnia and the Barbara streams have areas of 3.67 km^2 and 6.27 km^2, respectively. The direct catchment of the reservoir, with an area of 1.16 km^2, plays minor part in supplying water. The dam lifted the level of water in the valley in a 600-metre-long section. The average width of the reservoir is 310 m, and the average depth is 8 m.

The area of the catchment under discussion is almost completely afforested, and within it, there is forest nature reserve “Stok Szyndzielni” with the area of 54.96 ha. Vegetation in the catchment is mainly represented by: upper-zone spruce forest, lower-zone fir-spruce forest, acid beech wood, fertile Carpathian beech wood, and mountain sycamore wood. The only elements of infrastructure within the catchment are a forester’s lodge and a hiking-cycling trail. Along the divide of the catchment run walking tourist trails. Traffic of private cars is forbidden in the surrounding of the reservoir. The reservoir is not accessible for recreation (swimming or sunbathing) – its only function is to provide water, which excludes any other possible ways of use. The whole area of the catchment is supervised by the Bielsko Forest Inspectorate. Forest works are carried out complying with the principles of sustainable forest management [10]. As the result of the mentioned preconditions, there are hardy any chances for man to contaminate the environment. The atmosphere may be a potential source of contamination of water in the catchment because deposition of substances from the atmosphere concerns even regions that are located long distance away from the emitter [11]. The catchment under discussion is situated near the Upper-Silesian conurbation and the Ostrava industrial region.

The research that was carried out showed that water retained in Wapienica reservoir is of good quality. The values of physiochemical parameters (Table 1) were generally at levels typical of pure water [12, 13]. Little amounts of organic matter were reflected in low values of BOD_5 (maximum 2.4 mgO_2/dm^3) and COD (below 10 mg O_2/dm^3). Low

Table 1

Qualitative parameters of water in Wapienica reservoir between IX 2011 and VI 2012 (basing on data from AQUA S.A.) compared to parameters of waters classified as pure [12, 13]

Parameter	Unit	Wapienica Reservoir		Clean water
		Minimal value	Maximal value	
Reaction pH	—	6.9	7.7	6.0–8.5
Suspension	mg/dm^3	< 5.0	< 5.0	< 25
Dissolved oxygen	mgO_2/dm^3	8.8	12.1	> 8
BOD_5	mgO_2/dm^3	< 0.5	2.4	< 3
COD_{Mn}	mgO_2/dm^3	1.14	2.12	< 6
COD_{Cr}	mgO_2/dm^3	< 10.0	< 10.0	< 25
Conductivity	µS/cm	68.34	186.40	< 200–300
Calcium	$mgCa/dm^3$	8.81	25.90	< 100
Magnesium	$mgMg/dm^3$	1.26	4.42	< 50
Chlorides	$mgCl^-/dm^3$	< 5.0	< 5.0	< 200
Fluorides	mgF^-/dm^3	0.07	0.28	< 1
Sulphates	$mgSO_4^{2-}/dm^3$	7.2	20.5	< 150
Ammonia	$mgNH_4^+/dm^3$	< 0.1	< 0.1	< 1
Nitrates(III)	$mgNO_2^-/dm^3$	0.002	0.011	< 0.02
Nitrates(V)	$mgNO_3^-/dm^3$	2.6	5.0	< 10
Phosphates	$mgPO_4^{3-}/dm^3$	< 0.02	0.09	< 0.2
Manganese	$mgMn/dm^3$	< 0.010	0.018	< 0.1
Aluminum	$mgAl/dm^3$	< 0.020	0.486	< 0.5
Barium	$mgBa/dm^3$	0.015	0.036	< 0.1
Iron	$mgFe/dm^3$	0.086	0.170	< 1
Zinc	$\mu gZn/dm^3$	< 20	28	< 15
Copper	$\mu gCu/dm^3$	< 20	< 20	< 2–3
Chromium	$\mu gCr/dm^3$	< 5	6	< 20
Nickel	$\mu gNi/dm^3$	< 2	< 2	< 3
Lead	$\mu gPb/dm^3$	< 5	11	< 3
Cadmium	$\mu gCd/dm^3$	< 1	< 1	< 0.15
Cobalt	$\mu gCo/dm^3$	< 10	10	< 0.1

concentration of dissolved mineral substances was reflected in specific conductance at several dozen, maximum 186 μS/cm. What suggested good conditions for decomposition of contaminants was high concentration of dissolved oxygen (between 8.8 and 12.1 mgO_2/dm^3). Low amounts were reported for chlorides (below 5 $mgCl^-/dm^3$) and sulfates (maximum 20.5 $mgSO_4^{2-}/dm^3$), as well as biogenic compounds of nitrogen and phosphorus. Nitrates(V) were reported in amounts between 2.6 and 5.0 $mgNO_3^-/dm^3$, and phosphates occurred at maximum level of 0.09 $mgPO_4^{3-}/dm^3$. Low level of fertility of water in the reservoir is confirmed by the species composition of the phytoplankton existing in the reservoir. Research by Jachniak and Kozak [14] shows that it is characteristic of oligotrophic water, with average contents of biomass at 0.7 mg/dm^3, which classifies the reservoir as one showing oligo/mesotrophic properties.

While analyzing the quality of water in Wapienica reservoir, it is worth discussing the concentration of heavy metals. Their presence best reflects the degree of anthropogenic impact, because they are mainly introduced into the environment as a result of human activities [15–17]. The research showed anthropogenic influence on the environment within the catchment, because concentrations of zinc and lead reported in water samples periodically exceeded levels typical of non-contaminated natural waters (Table 1). Cobalt occurred in significant amounts, but it might occur naturally. Also, presence of high amounts of copper and cadmium is possible, but the scope of precision of the analytical methods that were used makes the assessment impossible. The analyses did not show presence of chromium or nickel in amounts that would suggest contamination with these elements.

Maximum concentration of zinc in analyzed water was 28 $\mu g/dm^3$. Zinc is easily distributed in the environment and its sources include mainly mining and metal processing. Generally, toxicity of zinc in water is not high. It is estimated that the metal shows toxicity for fish in case of concentrations exceeding 100 $\mu g/dm^3$ [12]. Lead occurred in maximum concentration at 11 $\mu g/dm^3$. This element is not easily distributed in soils, and in water environment it is often completely adsorbed in deposits. High concentrations of lead in the environment are usually related to industrial pollution and use of roads. At one time, the concentration of lead in water of Wapienica reservoir exceeded the value of 5 $\mu g/dm^3$, which is regarded as the safety threshold for water biocenoses [12]. Cobalt occurred in maximum amounts of 10 $\mu g/dm^3$. Such concentration is not a threat for water organisms, though. Toxic impact of cobalt starts with high concentrations, for example several dozen mg/dm^3 in case of fish [12]. Whereas occurrence of zinc and lead in water of the researched reservoir probably results from atmospheric deposition in the area of the catchment, presence of cobalt might also be, to a high extent, an effect of natural denudation of rock layers. This is so because the lithosphere usually plays a larger part as a source of cobalt than human activity [18].

The research also included studies of occurrence of some microorganisms in water of the reservoir. *Escherichia coli* occurred in the maximum amount of 21 organisms in 100 cm^3 of water, and the maximum amount of coli bacteria was 240/100 cm^3. No salmonella bacteria were discovered. Enterococci were present at one time, in the amount of 12 microorganisms in 100 cm^3 of water, whereas *Clostridium perfringens* were discovered in the maximum amount of 4 organisms per 100 cm^3 of water. The mentioned microorganisms are neutralized in the process of water treatment before it is directed to the water supply system. Treatment includes filtering water through anthracite-sand filters and disinfection with sodium hypochlorite [19].

Water treatment station for Wapienica reservoir is situated in its close vicinity. The fact that only basic treatment processes are used results from high quality of water. Classification of water quality according to the requirements for its treatment is carried out according to the respective Ordinance of the Minister of Environment, basing on values of 44 qualitative parameters of water [20]. Pure water is included in category A1 and it only requires basic physical treatment, especially filtration and disinfection.

Table 2

Surface water quality classification according to the requirements for treatment for consumption

Parameter	Unit	Water quality category [20]			Wapienica reservoir category
		A1	A2	A3	
Reaction pH	—	6.5–8.5	5.5–9.0	5.5–9.0	A1
Suspension	mg/dm^3	< 25	< 30	< 35	A1
Dissolved oxygen	mgO$_2$/dm^3	no restrictions			—
BOD$_5$	mgO$_2$/dm^3	< 3	< 5	< 7	A1
COD$_{Mn}$	mgO$_2$/dm^3	no restrictions			—
COD$_{Cr}$	mgO$_2$/dm^3	< 25	< 30	< 30	A1
Conductivity	µS/cm	< 1000	< 1000	< 1000	A1
Calcium	mgCa/dm^3	no restrictions			—
Magnesium	mgMg/dm^3	no restrictions			—
Chlorides	mgCl$^-$/dm^3	< 250	< 250	< 250	A1
Fluorides	mgF$^-$/dm^3	< 1.5	< 1.5	< 1.5	A1
Sulphates	mgSO$_4^{2-}$/dm^3	< 250	< 250	< 250	A1
Ammonia	mgNH$_4^+$/dm^3	< 0.5	< 1.5	< 2.0	A1
Nitrates(III)	mgNO$_2^-$/dm^3	no restrictions			—
Nitrates(V)	mgNO$_3^-$/dm^3	< 50	< 50	< 50	A1
Phosphates	mgPO$_4^{3-}$/dm^3	< 0.4	< 0.7	< 0.7	A1
Manganese	mgMn/dm^3	< 0.05	< 0.1	< 1	A1
Aluminum	mgAl/dm^3	no restrictions			—
Barium	mgBa/dm^3	< 0.1	< 1	< 1	A1
Iron	mgFe/dm^3	< 0.3	< 2	< 2	A1
Zinc	µgZn/dm^3	< 3000	< 5000	< 5000	A1
Copper	µgCu/dm^3	< 50	< 50	< 500	A1
Chromium	µgCr/dm^3	< 50	< 50	< 50	A1
Nickel	µgNi/dm^3	< 50	< 50	< 200	A1
Lead	µgPb/dm^3	< 50	< 50	< 50	A1
Cadmium	µgCd/dm^3	< 5	< 5	< 5	A1
Cobalt	µgCo/dm^3	no restrictions			—

Water of poorer quality (category A2) needs wider scope of physical and chemical treatment, especially pre-oxidation, coagulation, flocculation, decantation, filtration and disinfection in the form of final chlorination. Water included in category A3 requires advanced physical and chemical treatment using processes of oxidation, coagulation, flocculation, decantation, filtration, adsorption with activated carbon, and disinfection by means of ozonation and final chlorination. Surface water whose parameters exceed thresholds for category A3 cannot be taken from the environment for consumption purposes. Basing on the analyses that were carried out, water in reservoir Wapienica can be classified in category A1 (Table 2).

Apart from filters and disinfection devices, the water treatment station also includes the section for coagulation processes. The process is used periodically, in cases of high turbidity of water in the reservoir (exceeding 25 NTU) and is aimed at eliminating suspended matter along with absorbed contaminants. Coagulation is carried out before water intakes of filters (in distributing channels), using coagulant PAX 18. It is water solution of polyaluminium chloride. It should be mentioned that in the research, turbidity of water in the reservoir ranged between 0.83–3.6 NTU. Turbidity only increased in flood-like situations. In regular conditions, when the research was carried out, the concentration of suspended matter did not exceed 5 mg/dm^3, and maximum contents of dissolved substances reached only 117 mg/dm^3.

The above discussion regarding water treatment shows that water supply basing on resources from highly natural areas is a favorable solution in economic terms. This is so because treatment of polluted water involves use of expensive technologies. In case of reservoir Wapienica, maintaining its catchment in its natural state is the only guarantee for low-cost use of its retained water.

Conclusions

1. The catchment of reservoir Wapienica is a natural mountain catchment and human activity within its area is limited to sustainable forest management.
2. Water retained in the reservoir generally presents favorable physiochemical parameters, which results from lack of sources of contamination within the area of the catchment. Water quality according to requirements for treatment falls into category A1; thus before being transferred to the water mains network, only processes of filtration and disinfection are used.
3. Presence of zinc and lead in water of the reservoir, in concentrations exceeding the levels that are typical of non-contaminated natural waters, suggests anthropogenic influence, probably through atmospheric deposition.
4. Water environment of unmanaged mountainous regions of southern Poland may be contaminated with trace elements.

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JAKOŚĆ WÓD RETENCJONOWANYCH W NATURALNEJ ZLEWNI GÓRSKIEJ (ZBIORNIK ZAPOROWY WAPIENICA)

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Abstrakt: Badano jakość wód w zbiorniku zaporowym Wapienica. Próby pobierano w okresie od września 2011 r. do czerwca 2012 r. Zbiornik pełni funkcję zaopatrzenia w wodę pitną miasta Bielsko-Biała. Zlewnia zbiornika ma charakter naturalnej zlewni górskiej, pozbawionej wewnętrznych źródeł zanieczyszczenia. Uwarunkowania środowiskowo-organizacyjne decydują o dobrej jakości wody w zbiorniku. Woda charakteryzuje się niewielką ilością zawiesiny i substancji rozpuszczonych, korzystnymi warunkami tlenowymi oraz małą żyznością. Nie stwierdzono także zanieczyszczenia substancjami organicznymi. Woda retencjonowana w zbiorniku ma kategorię jakości A1, a zatem jej uzdatnianie może być ograniczone do filtracji i dezynfekcji. Analizy wykazały obecność niektórych metali ciężkich (Zn, Pb, Co) w ilościach przekraczających poziomy charakterystyczne dla niezanieczyszczonych wód naturalnych. Podwyższone zawartości cynku i ołowiu mogą być efektem depozycji atmosferycznej zanieczyszczeń, natomiast pochodzenie kobaltu może mieć charakter naturalny. Z badań wynika, że niezagospodarowane tereny górskie Polski południowej mogą być zanieczyszczone pierwiastkami śladowymi.

Słowa kluczowe: środowisko wodne, zbiornik zaporowy, zlewnia górska, użytkowanie terenu, jakość wody, metale ciężkie

DOI: 10.2428/ecea.2013.20(04)046 ECOL CHEM ENG A. 2013;20(4-5):491-502

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HYDROLOGICAL CONDITIONS IN SMALL-SCALE RETENTION BASINS RESTORED IN RURAL AREAS

WARUNKI HYDROLOGICZNE W ZBIORNIKACH MAŁEJ RETENCJI ODTWORZONYCH NA OBSZARACH WIEJSKICH

Abstract: This paper discusses the results of a hydrological survey of small-scale retention basins, including three lakes in a cascade system which were created by a dam on the Setal Stream and three smaller basins which were filled due to a rise in groundwater levels after the construction of weirs. All basins occupy an agricultural catchment in the municipality of Dywity (Olsztyn Lakeland). They are characterized by a small surface area (1–41 ha) and a shallow depth (1.6–3.6 m).

The objective of this study was to analyze water level variability and determine the retention capacities of the examined basins. The survey covered three hydrological years between 2005 and 2007. Water levels were monitored on a weekly basis. Retention capacities were determined from bathygraphic curves for average water levels (based on bathymetric maps which were developed for the needs of the study).

An analysis of the retention capacities of the studied basins during winter and summer points to higher levels of water accumulation in winter in all reservoirs. Lower retention in summer can be attributed to high ambient temperatures which speed up water evaporation and actual evapotranspiration from aquatic vegetation. The differences observed between the summer seasons in the analyzed hydrological years (other than evaporation which lowers retention) indicate that summer precipitation levels significantly affect retention capacity. The difference in the overall volume of water retained in all basins between the "dry" year of 2005 and the "wet" year of 2007 reached 104,600 m^3. Total winter retention during the three-year survey was determined at 1,511,600 m^3, and it was 69,700 m^3 higher in comparison with summer retention. The greatest fluctuations in the volume of retained water were noted in closed basins. In one of the studied reservoirs, a nine-fold difference was observed between the minimum and maximum retention levels.

Keywords: restored retention basins, small-scale water retention, water damming

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Introduction

Water resources in farmlands and forests are created by atmospheric precipitation (rain, snow) whose intensity varies in time and space. Small-scale retention basins are build to reduce water deficits. The aim of small-scale retention projects is to maximize the volume of accumulated water resources, mainly by slowing down water flows in micro-catchments. The retention capacity of a river catchment varies in time and space. Small-scale retention projects involve various measures, but they are generally associated with the construction of basins that retain surface waters [1–3]. In the region of Wielkopolska, small-scale water retention projects were carried out to recreate rural ponds and build dams on lakes and rivers. Those efforts led to the creation of water retention basins with total retention capacity of 97 million m^3 [3].

The restoration of water reservoirs is one of the measures that increase retention capacity. Lake damming, retention reservoirs [2, 4, 5] and series of cascade basins created by dams significantly improve the water balance [6, 7]. Retention basins which are an element of a lake and river network are an important feature of the post-glacial landscape. Basins accumulate surface and underground water from both shallow and deeper water-bearing horizons [8].

To optimize water retention, unproductive spring runoffs produced by melting snow are accumulated in midfield ponds, and retained water can be used during the growing season [2]. The majority of ponds accumulating drainage water are situated in agricultural land in close proximity to farm buildings. Many retention ponds were specially designed or adapted for fire fighting, farming or recreational purposes. Although their initial function has been lost, they continue to play an important role as extensive water retention reservoirs.

The vast majority of small-scale retention ponds are shallow basins without thermal stratification throughout most of the year. The accumulation of water from agricultural areas poses a significant threat for retention basins. Water runoffs from farmlands are characterized by high nutrient concentrations which contribute to eutrophication. This danger is particularly eminent in basins formed by dams where rapid deposition of bottom sediments creates an additional problem [6–8]. In basins which have no flows throughout most part of the year (excluding overbank flows caused by flooding) and are characterized by low water renewal rates, the surface layer is much more transparent in comparison with regularly supplied basins. The above can be attributed to the deposition of fine sediments despite generally higher trophy levels in closed basins.

The main goal of water resource management policies is to reduce water deficits, alleviate the consequences of droughts and improve water quality. Small-scale retention projects effectively minimize water deficits, in particular in farmlands and forests.

Materials and methods

The hydrological survey involved observations of six small-scale retention basins. The survey covered three hydrological years between 2005 and 2007. The main aim of the study was to analyze water level variability and determine the retention capacities of

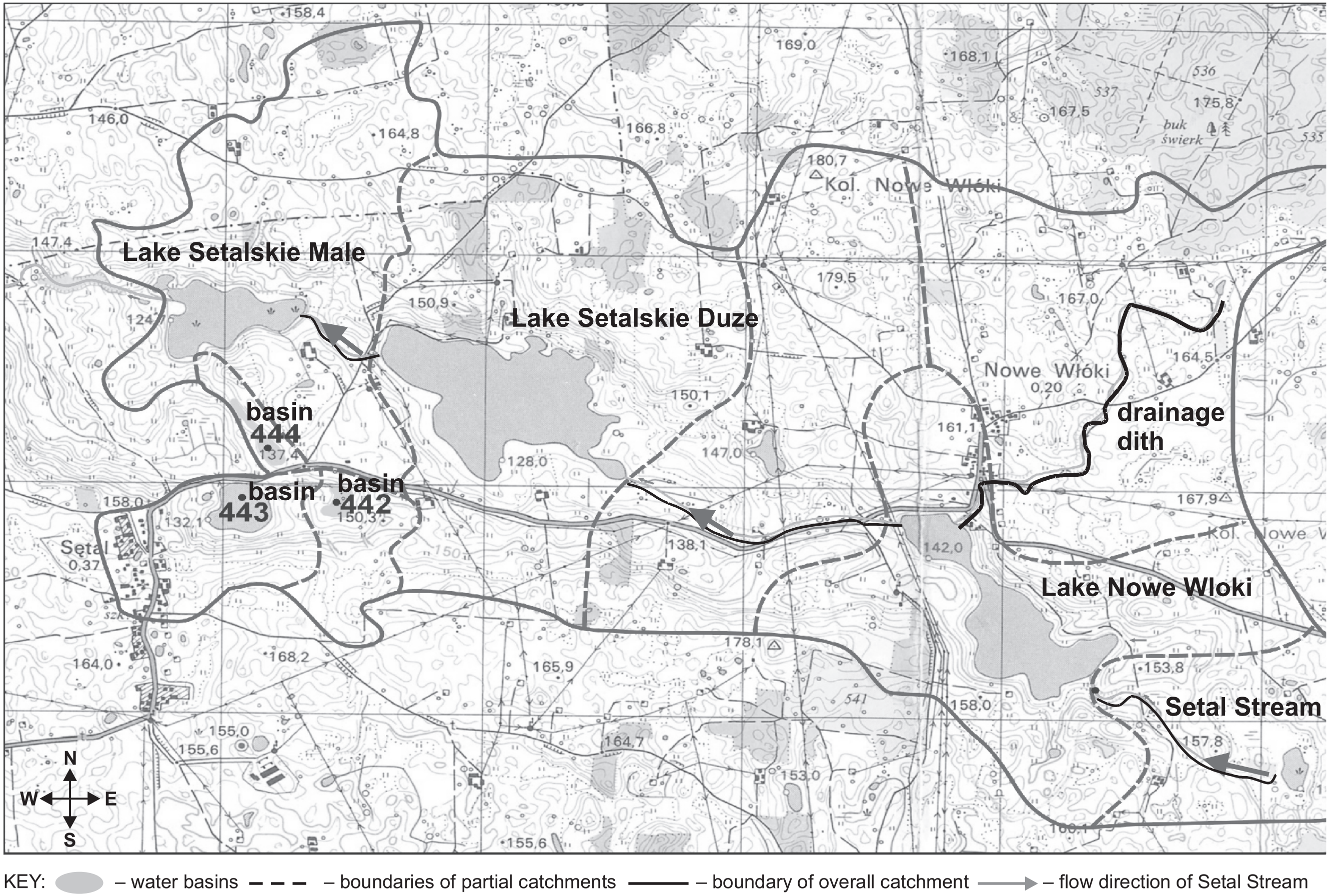

Fig. 1. Reconnaissance map of the studied basins and their catchment area

the examined basins across different years and seasons of the survey. The retention capacities of the analyzed reservoirs were also expressed per unit of catchment area.

Water levels were measured once a month using staff gauges. The zero point of the gauge was set at the bottom of the basin (in its deepest point). The volume of retention basins was determined from bathygraphic curves at average water levels. Bathymetric maps were developed in the Surfer application based on the results of field measurements. Bathygraphic curves were plotted in Excel 2007. In areas delimited by isobaths, volume calculations (in hectares) for plotting bathygraphic curves were performed in ImageJ image processing program. The volume of retention basins was calculated by the method proposed by Penck as the sum of partial volumes in areas enclosed by successive isobaths, and it was expressed in terms of thousands of m^3.

The analyzed retention basins are situated in Setal and Nowe Wloki in the municipality of Dywity. In the 19^{th} century, they were dried as part of a land reclamation program, and converted to grasslands. Due to a rising demand for water retention basins, the initial function of the analyzed reservoirs was restored in the 1970s and 1980s. The evaluated basins comprise three flow-through lakes of Nowe Wloki, Setalskie Duze and Setalskie Male (in the above order in a system of interconnected water bodies) situated along the Setalski Channel (a drainage channel currently referred to as the Setal Stream), which were created as a result of channel damming, as well as three closed basins which were filled due to a rise in groundwater levels, marked as basins No. 442, 443 and 444 in the survey. In the north, Lake Nowe Wloki is additionally supplied by a drainage ditch which evacuates water from Nowe Wloki, a village without a sewer system (Fig. 1).

The first tree reservoirs connected by the Setal Stream are a series of graduated cascade basins which occupy an area with significant differences in slope (3 to 6.6 5). Their surface area ranges from 8 to 41 ha, and their maximum depth reaches > 4 m (Table 1). The basins' total catchment area (calculated incrementally for successive lakes) was determined at 883.82 ha, including 408.19 ha for Lake Nowe Wloki, 349.04 ha for Lake Setalskie Duze and 126.59 ha for Lake Setalskie Male.

Table 1

Morphometric parameters of the studied basins

Basin	Area P [ha]	Depth [m]		Depth indicator D_{avr}/D_{max}
		D_{max}	D_{avr} V/P	
Flow-through lakes				
Lake Nowe Wloki	19.670	2.7	1.49	0.55
Lake Setalskie Duze	41.436	3.6	2.27	0.63
Lake Setalskie Male	8.075	2.6	1.11	0.43
Closed basins				
442	1.344	1.6	0.50	0.31
443	3.186	1.6	1.10	0.69
444	1.142	1.8	1.04	0.58

The three closed basins (442, 443, 444) are characterized by a much smaller surface area of 1 to 3 ha and a maximum depth of < 2 m (Table 1). They are situated in an area with significant differences in slope (5.7 – 7.7 %), and their catchments have an area of 22.5, 37.65 and 7.13 ha, respectively.

Results and discussion

Water level variations in the studied basins

During the three-year hydrological survey, the analyzed retention basins were characterized by significant variations in water level (Fig. 2, Table 2) and instantaneous maximum depth (the zero point of the staff gauge was set at the bottom of the basin at its deepest point). The greatest water table fluctuations of more than 100 cm were noted in closed basins (442 and 444) which are characterized by the smallest surface area of slightly above 1 ha. A maximum difference of 124 cm was reported in basin 442 which is situated in an open field with few trees or shrubs. The lowest water level noted during the study (107 cm) was also observed in basin 442. Due to its location, this basin was highly susceptible to drying at high summer temperatures (Fig. 2). The results of other research studies also indicate that shallow water reservoirs rapidly respond to environmental changes, in particular weather conditions [9–11]. When ambient temperatures increased in spring, water levels in basins 442 and 444 rose dramatically due to higher supply of melt water and intense precipitation. In spring, the average water table elevations (2005–2007) in basins 442 and 444 were 20 cm higher than in winter. In basin 443, the average altitude of the water table was 5 cm lower than in winter, which could be attributed to the outflow of groundwater from the basin to a drainage ditch in its vicinity. Basin 443 was also characterized by the lowest fluctuations in water levels which were determined at 30 cm (Table 2).

The highest water levels were generally observed in spring in all analyzed basins. In larger flow-through lakes, the differences in water table elevation relative to the winter season were not as pronounced as in closed basins, and they reached 3 cm in Lake Nowe Wloki, 4 cm in Lake Setalskie Duze and 11 cm in Lake Setalskie Male (Table 2). In spring, the highest water table in Lake Setalskie Male can be attributed to high inflow per unit area from the Setal Stream (average of 6.45 $\mathrm{dm^{-3} \cdot s^{-1} \cdot km^{-2}}$). The stream connects Lake Setalskie Duze with Lake Setalskie Male which is situated at the lowest altitude in the examined catchment.

The type of reservoir significantly contributes to changes in water level. Closed basins which are much shallower than flow-through lakes were characterized by considerably greater fluctuations in water table elevation. In summer, the water table was lower in all basins when high ambient temperatures increased the rate of evaporation and intensified evapotranspiration in comparison with other seasons of the year (Fig. 2, Table 2).

In the hydrological years of 2005–2007, water levels remained fairly constant, and less profound fluctuations were observed in lakes Nowe Wloki and Setalskie Duze, probably due to the high altitude of their outflows. A similar trend was noted in basin

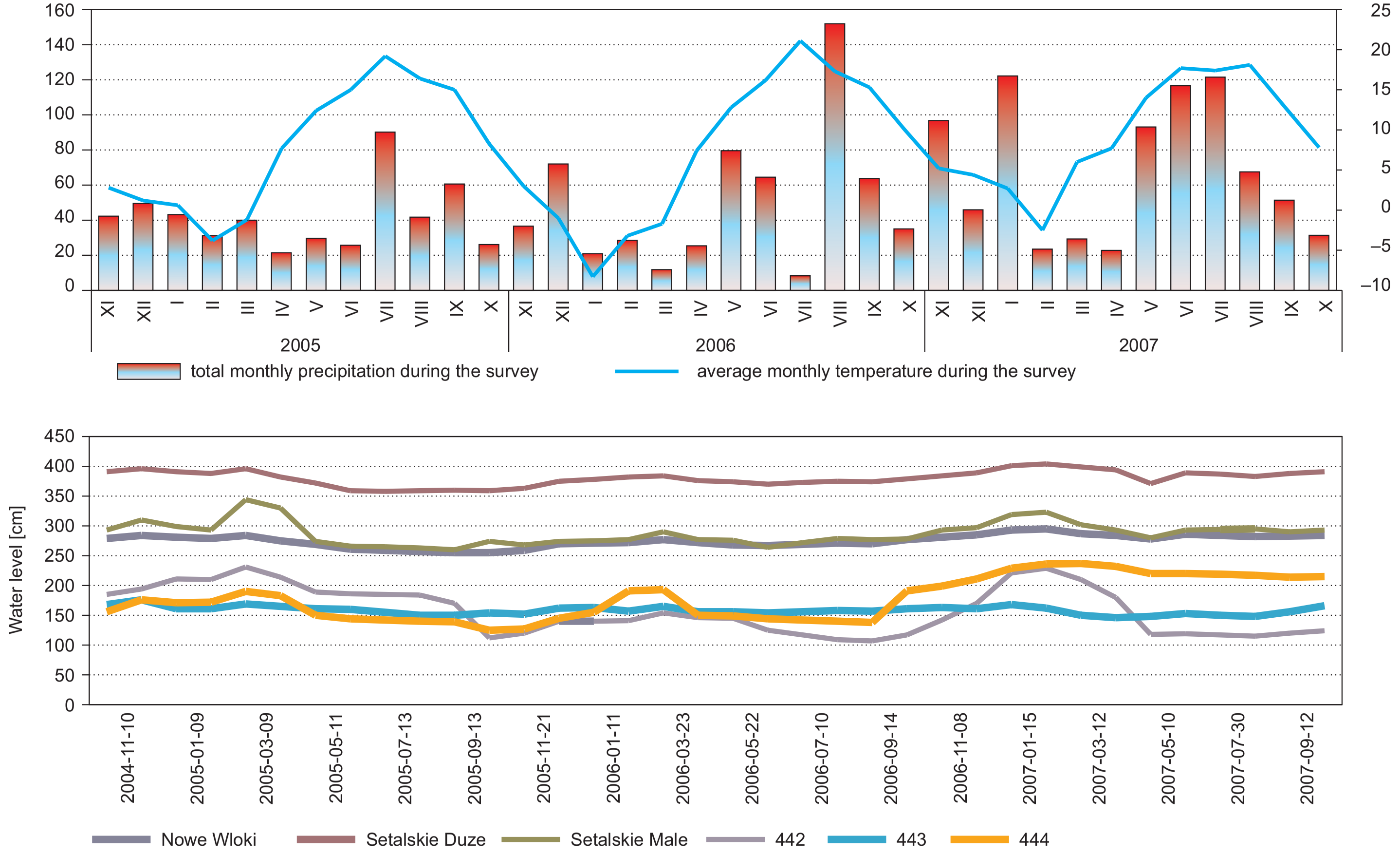

Fig. 2. Water table fluctuations (corresponding to the maximum depth of retention basins) in 2005–2007 as a function of precipitation volume and ambient temperature

Table 2

Water table fluctuations during the survey and average water levels in each season

Basin	Water level [cm]				Average water levels in seasons			
	min	max	average	amplitude	winter	spring	summer	autumn
Flow-through lakes								
Lake Nowe Wloki	255	295	275	40	278	281	271	269
Lake Setalskie Duze	359	404	380	45	385	389	373	374
Lake Setalskie Male	260	344	287	84	292	303	276	278
Closed basins								
442	107	231	159	124	169	191	145	132
443	146	176	158	30	164	159	155	155
444	125	237	177	112	174	198	170	165

443. Two distinct tendencies can be identified in the three-year period of the study. Years 2005 and 2007 were characterized by similar retention patterns in spring. A more rapid increase in water levels was observed during that season, which can be attributed to melt water inflows, above-zero temperatures and intense precipitation in the winter months (January and February) of 2005. In the hydrological year of 2007, abundant rainfall was reported already in November, which gradually increased water levels to reach a maximum in spring. A different tendency was reported in the hydrological year of 2006. In all basins (excluding 444), less intense changes in water table elevation were noted in spring due to lower precipitation in January (20.9 mm), February (28.5 mm) as well as the autumn months (October, November) of 2005. For this reason, the increase in basin volume was considerably lower than in the remaining years of the study. Melt water inflows merely supplemented water losses sustained in summer. In spring, a significant increase in water levels in basin 444 could probably also be attributed to considerable differences in slope (7.7 %) which intensified surface inflows (Fig. 2).

Our observations suggest that high precipitation levels in the autumn months contribute to the preservation of water levels, in particular in small and shallow water bodies. Abundant rainfall in autumn prevents water deficits which often follow after a period of intense evaporation and transpiration in summer. This phenomenon was observed in September 2005 in the smallest analyzed basins – 442 and 444.

An analysis of water table fluctuations in the studied basins indicates that water table stability is conditioned mainly by summer precipitation. Abundant rainfall prevents a drop in rapidly decreasing water levels. This was noted in the summer of 2007 in all water bodies (excluding basin 442) when despite high ambient temperatures, intense precipitation (116.6 mm in June, 121.5 mm in July, 67.5 mm in August) contributed to the maintenance of higher water levels in comparison with previous summers.

Retention capacity of basins

The volume of water basins (determined based on bathygraphic curves) at average water levels in the analyzed hydrological years and the mean values for the period of the study are presented in Table 3. The largest water resources were accumulated in Lake Setalskie Duze at 1,021,000 m^3 on average in the analyzed years, which was due to the reservoir's highest average depth of 3.8 m and its surface (43.2 ha on average). At the time of the highest water table (404 cm), the lake had an area of 44.6 ha, and it accumulated the maximum amount of water which was determined at 1,095,000 m^3. In the same period, Lake Nowe Wloki, which is twice smaller than Lake Setalskie Duze, retained 300,000 m^3 of water, and its storage capacity was determined at 325,000 m^3 during the highest water table (295 cm). Lake Setalskie Male, which is five times smaller than Lake Setalskie Duze in terms of surface area, stored ten times less water (103,500 m^3) than the latter.

Table 3

Retention capacities of the studied basins [in '000 m^3] – average values for each hydrological year and the entire period of study

Basin	Average retention in hydrological year			Retention during the study			
	2005	2006	2007	min	max	average	difference
Lake Nowe Wloki	294	291	314	267	325	300	58
Lake Setalskie Duze	1015	997	1050	935	1095	1021	160
Lake Setalskie Male	105	97.5	108	89	129.8	103.5	40.8
Basin 442	11.3	3.3	6.2	2.1	19.9	6.9	17.8
Basin 443	35.6	34.3	33.7	30.8	40.5	34.6	9.7
Basin 444	9.9	8.7	16.5	6.5	19.8	11.7	13.3
Total	1470.8	1431.8	1528.4	1330.4	1630.0	1477.2	—

In the group of three closed basins (442, 443 and 444) characterized by a small surface area (1 to 3 ha), the highest retention capacity was determined in basin 443 which accumulated 34,600 m^3 of water on average. Although basins 442 and 444 were similarly sized (area of approximately 1 ha), their retention capacities differed substantially. During average water table conditions (159 cm in basin 442 and 177 cm in basin 444), the retention capacity of basin 442 was nearly half that of basin 444 (Table 3).

The highest retention capacities in Lakes Setalskie Duze, Nowe Wloki, Setalskie Male and basin 444 were observed in 2007. Basins 442 and 443 accumulated the largest amounts of water in 2005. In all basins, the lowest water retention was noted in 2006. In that year, basins 442 and 444, the smallest reservoirs which are most sensitive to changes in weather conditions, accumulated nearly half the amount of water in comparison with other years of the study. Significant fluctuations in retention capacities resulted mainly from variable precipitation which increased in successive years of the study. Although total precipitation in the hydrological year of 2006 was higher (598.3 mm) than in the dry year of 2005 (501.6 mm), the investigated basins accumulated less water due to the need to make up for the loss of underground water resources caused by drought. The above also resulted from significant fluctuations in precipitation which reached the highest level in the growing season. In 2007, rainfall (822.0 mm) levels exceeded the multi-year average (1971–2000) by 197 mm, which contributed to the highest retention capacities (Fig. 2, Table 3). The greatest variations in retention capacity was noted in basin 442 where a nine-fold difference was reported between maximum and minimum accumulation levels. On average, the analyzed basins accumulated a total of 1,477,200 m^3 of water, where the resources of the flow-through Lake Setalskie Duze accounted for 69 % of the above.

All of the studied basins stored more water in winter (Table 4). Lower retention capacities in summer can be attributed to high ambient temperature, increased water evaporation and evapotranspiration of aquatic vegetation. The growth of rush plants (reeds and sedges) which have a high transpiration capacity also influences water accumulation [12]. In addition to evaporation rates which decrease retention capacity, an analysis of variations in the summer months of the studied hydrological years also points to the significant role of summer precipitation. The difference in water resources accumulated in the examined basins between the “dry” year of 2005 and the “wet” year of 2007 reached 104,600 m^3. During the study, the overall winter retention capacity of the analyzed basins was determined at 1,511,600 m^3 on average, which was 69,700 m^3 higher than in summer.

Table 4

Average retention capacities of the analyzed basins in the summer and winter months [’000 m^3]

Basin	Winter				Summer			
	2005	2006	2007	average	2005	2006	2007	average
Lake Nowe Wloki	307	290	316	304	280	293	312	295
Lake Setalskie Duze	1067	997	1068	1044	963	997	1032	997
Lake Setalskie Male	112	98.5	111	107	98.5	97	103.5	100
Basin 442	12.4	3.6	9.3	8.4	10.3	3.0	3.2	5.5
Basin 443	37.1	34.8	35.6	36	34.2	33.7	31.8	33.2
Basin 444	11.1	9.3	16.3	12.2	8.7	8.1	16.8	11.2
Total	1546.6	1433.2	1556.2	1511.6	1394.7	1431.8	1499.3	1441.9

The studied water basins had a highly varied share of total retention capacity per unit of catchment area (Table 5). In flow-through lakes, the noted differences resulted not only from their morphometric parameters, but also their sequence in the hydrological network and the resulting increase in catchment area. In the analyzed basins, the average retention ranged from 12 mm in Lake Setalskie Male to 135 mm in Lake Setalskie Duze. In the group of closed basins, the highest average retention capacity during the period of the study was noted in basin 444 at 164 mm, and the lowest – in basin 442 at 31 mm. In the majority of the studied reservoirs (excluding basins 442 and 443), the highest retention capacities were reported in 2007 when they exceeded the average values for the entire period of the study. In closed basins 442 and 443, retention capacities peaked in the first year of the experiment. In the analyzed hydrological years, the greatest fluctuations in retention capacities were noted in closed basins. In basin 442, a nine-fold difference was observed between minimum and maximum levels.

Table 5

Retention capacities per unit of catchment area [mm]

Basin	Average retention in hydrological years			Retention during the period of the study		
	2005	2006	2007	min	max	average
Lake Nowe Wloki	72	71	77	65	80	74
Lake Setalskie Duze	134	132	139	124	145	135
Lake Setalskie Male	11.8*	11	12.2*	10	15	11.7*
Total retention of flow-through lakes	160	157	167	146	175	161
Basin 442	51	15	28	10	90	31
Basin 443	95	91	90	82	108	92
Basin 444	139	122	231	91	278	164
Total retention of closed basins	85	69	84	59	120	80

In flow-through lakes, the catchment area was calculated incrementally based on their location in the hydrological network; * Retention values are given to the first decimal place due to small differences in volume.

Conclusions

The volume of water retained by the studied reservoirs was determined by weather conditions (precipitation and temperature) and the basins' morphometric features. The results of the study indicate that high precipitation levels in autumn contribute to the preservation of the water table, in particular in small and shallow water bodies. Low rainfall caused the most severe water deficits because intense evaporation and transpiration in summer contributes to low water levels in autumn. Similar observations were made by other authors [9–11]. Closed basins (excluding basin 443) with depths not exceeding 2 m were characterized by greater fluctuations in water table than flow-through lakes. The variations in water levels were significantly less pronounced in reservoirs with an outflow, which can be explained by the fact that hydrological conditions in water bodies are also determined by the type of water supply. In addition to rainfall, ground water and surface runoffs, watercourses are very important sources of supply. For this reason, the Setal Stream which flows through the analyzed lakes significantly minimized the fluctuations in their water table. Similar results were reported by Kanclerz et al [13] in a study of two large lakes connected by River Mała Wełna and by Korytowski [11] who investigated small closed basins.

The retention capacities of the studied water basins were determined by their morphometric parameters. In periods characterized by average water levels, flow-through lakes accumulated 103,500 to 1,021,000 m^3 and closed basins – from 6,900 to 34,600 m^3 of water, producing a total of 1,477,200 m^3. In view of the analyzed reservoirs' combined volume at average water levels, the average retention capacity per unit of total catchment area reached 161 mm in flow-through lakes and 80 mm in closed basins. In a study by Szyperek [9], ponds with a volume of 50 to 8,701 m^3 retained from 1.1 to 13.4 mm of water. The above results indicate that water bodies in the Olsztyn Lakeland are characterized by significantly higher retention capacity than reservoirs in other regions of the country. In our study, each of the six reservoirs retained three times more water on average than the basins (a total of 418) developed as part of a small-scale retention project in the Wielkopolska region [3]. Wielkopolska is situated in one of the lowest rainfall zones in the country, therefore, the results noted in that region are also indicative of its high retention capacity.

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WARUNKI HYDROLOGICZNE W ZBIORNIKACH MAŁEJ RETENCJI ODTWORZONYCH NA OBSZARACH WIEJSKICH

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Abstrakt: W pracy zaprezentowano wyniki badań hydrologicznych dotyczących zbiorników małej retencji – trzech powstałych w wyniku podpiętrzenia wody na Strudze Sętal i stanowiących układ kaskadowy oraz trzech mniejszych obiektów, które w wyniku zastosowanych zastawek napełniły się na skutek podniesienia poziomu wód gruntowych. Wszystkie akweny położone są na terenie gminy Dywity (Pojezierze Olsztyńskie), w zlewni o wyraźnym ukierunkowaniu rolniczym. Cechą charakterystyczną jest ich niewielka powierzchnia (1–41 ha) oraz głębokość (1,6–3,6 m).

Celem pracy była analiza zmienności stanów wód badanych zbiorników oraz określenie ich zdolności retencyjnych.

Wyniki są efektem trzyletnich badań, przeprowadzonych w latach hydrologicznych 2005–2007. Stany wód odczytywane były w cyklach cotygodniowych. Możliwości retencyjne zbiorników odczytywano z krzywych batygraficznych przy średnich stanach wód (sporządzonych na podstawie planów batymetrycznych, które również zostały wykonane w ramach prac badawczych).

Rozpatrując retencję zbiorników wodnych w okresie zimowym i letnim, zaobserwowano tendencję do gromadzenia większych zapasów wody we wszystkich zbiornikach – w półroczu zimowym. Niższe wartości w półroczu letnim wynikają z wysokich temperatur powietrza, co zwiększa procesy parowania wody, ale także ewapotranspiracji rzeczywistej roślinności pokrywającej zbiornik.

Analizując różnice występujące w półroczach letnich w latach hydrologicznych, zaznacza się (oprócz parowania, kształtującego niższą retencję wody) ogromne znaczenie opadów letnich. Różnica między rokiem „suchym” (2005) a „mokrym” (2007) w sumie wody zgromadzonej we wszystkich akwenach wyniosła 104,6 tys. m^3. Podczas trzech lat obserwacji w półroczu zimowym zbiorniki wodne zgromadziły średnio 1511,6 tys. m^3, czyli więcej o 69,7 tys. m^3 niż w półroczu letnim.

Wykazano, że najwyższe wahania w retencji wód wystąpiły w obiektach bez odpływu wody. W przypadku jednego z badanych akwenów, różnica między minimalną a maksymalną retencją była aż 9-krotna.

Słowa kluczowe: zbiorniki odtworzone, mała retencja, podpiętrzenie wód

DOI: 10.2428/ecea.2013.20(04)047 ECOL CHEM ENG A. 2013;20(4-5):503-514

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SPECIATION OF PHOSPHORUS IN WASTEWATER SEDIMENTS FROM SELECTED WASTEWATER TREATMENT PLANT

SPECJACJA FOSFORU W OSADACH ŚCIEKOWYCH Z WYBRANYCH OCZYSZCZALNI ŚCIEKÓW

Abstract: The aim of this work was to characterize wastewater sediments of various types of wastewater treatment plants in terms of the occurrence of forms of phosphorus speciation. The preliminary analysis of speciation using sequential extraction by Golterman was made.

It consists in using chelating reagents (Ca-EDTA and Na-EDTA) as well as NaOH and H_2SO_4 solutions. The quantitative measurement of phosphorus was carried out using spectrophotometric method according to binding rules. The number of individual fractions of phosphorus in wastewater sediments and the concentration of total phosphorus in treated and raw wastewater were examined. According to Golterman the phosphorus absorbed on the surface of sludge particles, so called mobile phosphorus, is a speciation form that is the most easily accessible for organisms. Preliminary results show that the significant participation of mobile phosphorus in wastewater sediments appeared in these wastewater treatment plants, where integrated methods of the wastewater treatment were applied (wastewater treatment plants mechanical-biological-chemical). The results obtained allow to conclude that, depending on the physico-chemical conditions in the various types of wastewater treatment plants, excess sludge shares have different forms of mobile phosphorus speciation, which may affect the recovery of this element from wastewater sediments.

Keywords: mobile phosphorous, wastewater sediments, speciation

Introduction

The growth of the standards of living, legal requirements posed to water treatment plants and the ecological education of the population cause an increasing amount of treated wastewater and the reduction of the amount of raw wastewater entering the environment [1]. This fact is beneficial in terms of the present water and wastewater management. However, the amount of wastewater sediments increases with the

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emergence of modern, high-qualified water treatment technologies. Wastewater sediments need to be well managed, because they are the source of many nutrients [2]. Phosphorus, which is one of them, is a major macro element that is necessary for the proper functioning of every cell. First of all phosphorous is a nucleic acid component and a high-energy bond component contained in the molecule of adenosine triphosphate (ATP), which is the primary source of energy for all biochemical reactions occurring in the living body [3]. The form of its occurrence in wastewater should be paid attention to because of the importance of this element to the environment [4]. Knowledge of the occurrence forms of phosphorus in wastewater sediments is important for understanding the bioavailability and mobility of this element in the soil [5, 6].

Speciation analysis determines the amount of phosphorous available to plants. This analysis is based on the procedures which permit the identification of the root forms and their quantitative determination of the examined object [7, 8]. According to the literature, several methods of speciation of phosphorus are known, where the sequential extraction is used [9]. Golterman method is one of them and originally it was used to analyze the speciation of elements in soils and sediments [9, 10] and also it has been used for the analysis of wastewater sediments in recent years [11]. This method involves the usage of chelating reagents (Na-EDTA and Ca-EDTA) sulfuric acid and sodium hydroxide solutions in the analysis. The use of chelating reagents allowed to shorten the time of the sequential analysis and prevented the change of the pH-value and thus the hydrolysis and dissolution of the phosphate. The extraction solvent combination allowed to isolate the phosphorus inorganic form (extracted using chelating reagents) and organic forms (extracted with solutions of NaOH and H_2SO_4). The author of the presented method has concluded that the greatest speciation bioavailability form is phosphorus adsorbed on the surface of the sediments particles, such as the fraction Ca-EDTA-P and fraction Na-EDTA-P [10, 12].

Table 1

Phosphorus fractions and their designations, according to Golterman method [9, 10, 12]

Stage	Type of extractant and extraction conditions	Fraction
1	0.05 M Ca-EDTA, 4 h	Ca-EDTA-P Phosphorus – associated with iron, aluminum and manganese oxides and hydroxyoxides
2	0.1 M Na-EDTA, 18 h	Na-EDTA-P Phosphorus – associated with carbonates
3	0.5 M H_2SO_4, 2 h	H_2SO_4-P Phosphorus presented with the soluble organic matter connection
4	2 M NaOH, 2 h	NaOH-P Remaining phosphorus in the association with aluminosilicates and contained in the form of organic matter undergoing no influence of sulfuric acid in stage 3

The content of inorganic phosphorus in sediments was estimated in range from 15 to 80 % of P_{org} [13]. According to other authors inorganic phosphorus content in wastewater sediments is considerably higher than the content of organic phosphorus [4, 14]. The aim of our work is to determine how the quantity of phosphorus speciation profile forms (in particular the bioavailable form) in wastewater sediments depending on their method of wastewater treatment.

Physical, biological or chemical methods are used for the phosphorus removal in wastewater treatment plants. The integrated wastewater treatment methods are used in modern wastewater treatment plants [15]. The biological method relies largely on the use of the ability of certain bacteria (for example of the *genus Acinetobacter, Pseudomonas*) to the enhanced retrieval of phosphate in the biochemical processes [16, 17]. Anaerobic or aerobic conditions are alternately applied to select and enable the development of specific cultures of bacteria [13, 18]. Chemical methods rely on precipitation of phosphates while using reagents such as precipitating ions of iron, aluminum or calcium [19]. The dephosphatation process causes the transition of the phosphorus in the form of intracellular polyphosphate (biological treatment) or in the form of sparingly soluble salts (chemical treatment) to the wastewater sediments [12].

The removal of biogenes in the process of biological wastewater treatment is strictly correlated with the amount and the metabolic activity of the microorganisms as well as with other factors like temperature [20], pH-value and the age of the sediment, the content of the nutritive substances and the oxygen [21]. The temperature of the surroundings is a significant parameter which influences the biological wastewater treatment because the bacteria involved in the reduction of the contamination develop only in an accurate range of temperature [22]. A substantial part of the population of the bacteria which appear in the wastewater sediments is constituted by the mesophiles, which develop in medium temperatures, that is in such a range of temperatures where the minimal temperature amounts to about 10 ^{o}C and the maximum temperature amounts to 45 ^{o}C. Parasitic microorganisms and a substantial part of saprophytes belong to this group of bacteria. The optimum of the growth ranges, according to the kind of bacteria, from 20 to 40 ^{o}C. Łomotowski and Szpindor [14, 22] present the influence of the temperature on the intensity of the biochemical processes in the wastewaters in the form of the exponential function equation:

$$k(t) = k_{20} \exp[K(t - 20)]$$

where: $k(t)$ – the constant of the biochemical processes speed in temperature t, ^{o}C;
k_{20} – the constant of the speed in temperature 20 ^{o}C;
K – temperature constant, $^{o}C^{-1}$.

The biological processes connected with the phosphorus removal are considered to be less sensitive to temperature changes. It is associated with the metabolism of the psychrophilic bacteria (which are responsible for the reduction of phosphorus in the wastewaters) developing in the lower temperatures that other organisms. The optimal temperature in the dephosphation processes is included within the range from 10 to 15 ^{o}C. However, literature signals that during winter the temperature of the sediments in the open containers may amount to 5 ^{o}C. The metabolic activity of the phosphoric bacteria slows down which results in decrease of the intensity of the enzymatic hydrolysis process. Then, together with the decrease of the sediment temperature, the speed of the endogenous decomposition of organic compounds is reduced which causes the increase of organic substance in the activated sludge [23].

Material and methods

The study was performed on the wastewater (raw and treated) and the excess sediment derived from the three wastewater treatment plant such as:

– Radoszyce – which applies mechanical and biological treatment; biological treatment is based on a three-phase activated sludge method (with separate zones: anaerobic and aerobic oxygenated).

– Barcza – where a mechanical-biological and chemical treatment is used. The technology is a combination of the three-phase method of activated sludge and revolved biological field methods. Biological phosphorus removal process is aided by chemical precipitation process coagulant PIX.

– Bartkow – where a mechanical-biological and chemical treatment is used. The biological treatment of sewage sludge phase method and the chemical treatment is carried out by means of the precipitating agent which is calcium.

The content of phosphorous fraction in collected excess sludge samples was specified by means of the fractionation scheme proposed by Golterman [12, 24]. The first stage constituted extraction with solution of Ca-EDTA for a period of 4 hours. In the second stage, the samples were extracted for 18 hours with a solution Na-EDTA. The next stage was the extraction of the sample for the period of 2 hours with a solution of H_2SO_4. The final stage also lasted 2 hours and NaOH solution was used for the extraction. Every sample was filtered after each extraction stage and the precipitate remaining after filtration was treated with the following reagents in the order of extraction. The concentration of orthophosphate and total phosphorus was measured in obtained filtrate. Spectrophotometric method was used to determine the concentration of phosphorous in wastewater and in sediments extractions. Marcel Media UV/VIS Spectrophotometer was employed. These measurements were repeated in three series and held in accordance to the determination of orthophosphate with blue phosphate – molybdenum and with the determination of total phosphorous after oxidation of the sample with potassium persulphate(VI) solution [25]. The research was repeated in three series in one-year cycle, where average temperatures during the sample collection in spring, summer, autumn and winter amounted to respectively 16 ^{o}C, 25 ^{o}C, 8 ^{o}C, –2 ^{o}C.

Results and discussion

The obtained results of phosphorus concentration in the treated and raw wastewaters lead to a conclusion that the highest degree of the removal of the element from selected objects was found in wastewater treatment plants Barcza and Bartkow (Fig. 1).

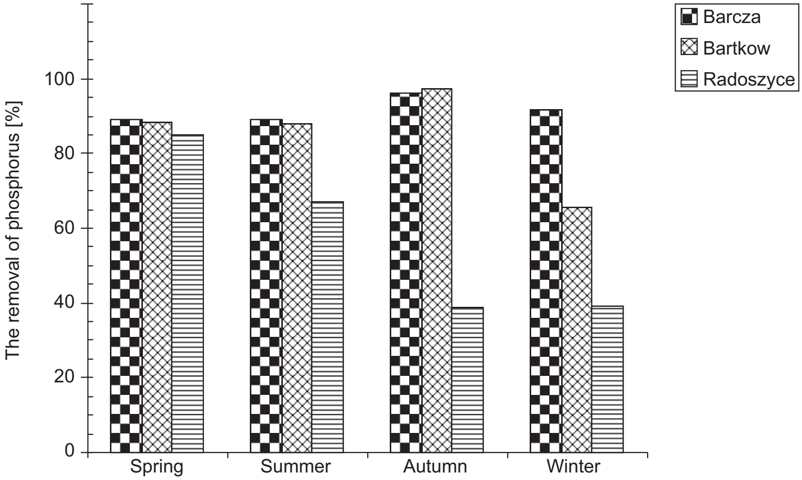

Fig. 1. The percent of total phosphorus removal in selected wastewaters treatment plants

The percentage of total phosphorus in the wastewater in wastewater treatment plant in Barcza in one-year cycle is almost constant and equaled about 90 %. In the case of wastewater treatment plant in Bartkow in the period of spring, summer and autumn the percentage of total phosphorus removal in the wastewater was also high and fluctuated around 90 %, while in winter it dropped distinctly and amounted to 66 %. The lowest percentage of total phosphorus removal was observed in the wastewater treatment plant in Radoszyce. The highest percentage of the removal in this object was observed in autumn and winter and fluctuated around 39 %. The above mentioned results which

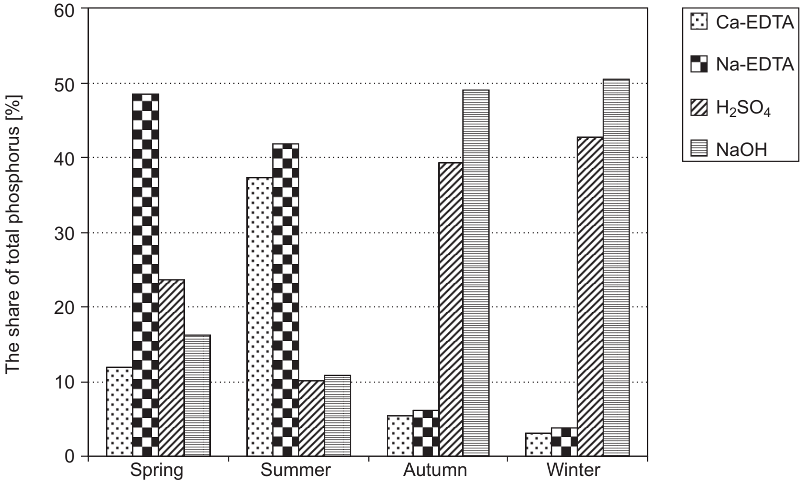

Fig. 2. The percentage share of the total phosphorus fraction in the excess sediment from the wastewater treatment plant in Bartkow in a one-year cycle

show the degree of phosphorus reduction in the wastewater can be linked to phosphorus efficiency of the process conditions in the wastewater treatment plant. It can be concluded that the more extensive the combination of wastewater treatment systems is the bigger the percentage of phosphorus reduction in the wastewater is.

The analysis of the results of phosphorus speciation marked as total phosphorus in a one-year cycle in the excess sediment from the wastewater treatment plant in Bartkow shows that in the spring-autumn period dominated the bioavailable fractions (Ca-EDTA and Na-EDTA), while in the autumn-winter period the shares of these fractions were reduced together with the drop of temperature of the surroundings. The dominating total phosphorus fractions in the autumn-winter period were H_2SO_4 and NaOH fractions, that is the organic phosphorus fractions (Fig. 2). Such a reversal of proportions between the shares of easily and not easily bioavailable phosphorus forms may result from the inhibition of biochemical processes of the microorganisms during winter, caused by the drop of temperature of their surroundings. The shares of the organic phosphorus forms are increased.

Similar results of the analysis may be observed in case of the excess sediments from the wastewater treatment plant in Barcza (Fig. 3) and in Radoszyce (Fig. 4) In the spring-summer period the bioavailable fractions (Ca-EDTA and Na-EDTA) were dominating, while in the autumn-winter period the organic phosphorus fractions (H_2SO_4 and NaOH) dominated. Despite the fact that each of the three wastewater treatment plants carries out the clearance of the wastewater on different levels of integrating the methods, the shares of the phosphorus fractions in the excess sediments from these wastewater treatment plants changes by analogy in a one-year cycle.

Then, it can be stated that together with the drop of temperature of the surroundings of the microorganisms, the metabolic activity of the phosphoric bacteria also slows down, which results in the intensity of the enzymatic hydrolysis decreases. In this

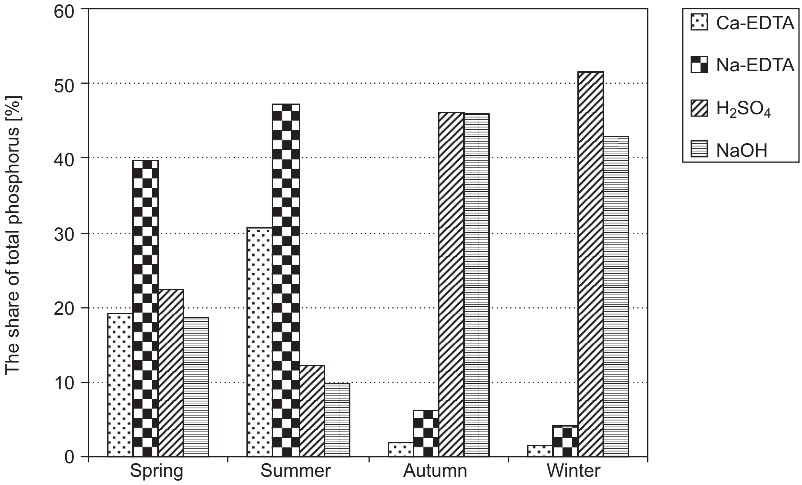

Fig. 3. The percentage of the phosphorus fraction in the excess sediment from the wastewater treatment plant in Barcza in one-year cycle

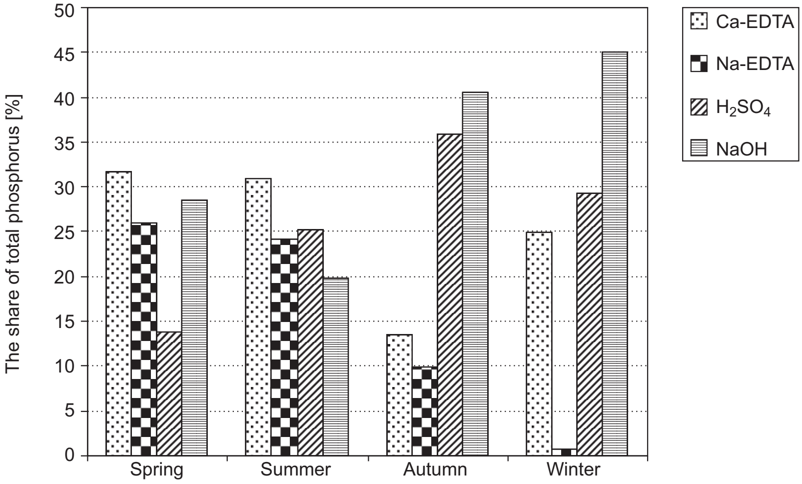

Fig. 4. The percentage of shares of the total phosphorus fractions in the excess sediment from the wastewater treatment plant in Radoszyce

connection, the drop of temperature of the sediment causes the reduction of the endogenous decomposition speed of the organic compounds, which causes the increase of the organic substance in the wastewater sediment.

The analysis of the results (Fig. 5) also showed that bigger disproportions between the shares of the bioavailable phosphorus forms in one-years cycle can be notices in the wastewater sediments from the wastewater treatment plants where the integrated methods of the wastewater treatment (mechanical-biological-chemical) are used. In case of the sediment from the wastewater treatment plant in Bartkow the sum of the percent

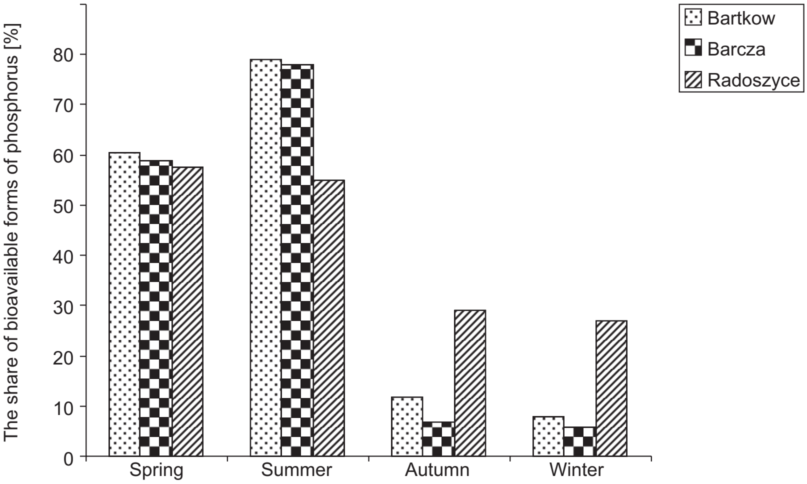

Fig. 5. The percent share of mobile phosphorus fractions in the excess sludge from the selected wastewater treatment plants

share of Ca-EDTA and Na-EDTA fractions amounted to in spring and summer 60 % and 79 % respectively, whereas in autumn and winter 12 % and 8 % respectively.

The drastic reduction of shares of the bioavailable forms in one-year cycle could be noticed also in the examined sediments from the wastewater treatment plant in Barcza. In the excess sludge from this wastewater treatment plant in spring and summer the total share of the bioavailable phosphorus forms amounted to 59 % and 78 % respectively, while the shares of these forms in autumn and winter equaled 7 % and 6 % respectively.

In case of the sediment from a mechanical-biological wastewater treatment plant in Radoszyce the sum of the percent share of the Ca-EDTA and Na-EDTA amounted to respectively 58 % and 55 % in spring and summer, while in autumn and winter equaled 29 % and 27 % respectively.

The statistic evaluation of the results of the phosphorus contents marking in the sediments expressed as total phosphorus, divided into fractions, obtained by means of the Goltermann method was based on the linear regression.

$$y = a \cdot x + b$$

where: y – dependent variable (the speciation of phosphorus in the wastewater sediments),
x – independent variable (the influence of the factor – air temperature),
a, b – parameters of the model,

In order to check the correctness of the model, the determination coefficients R^2 were determined. They describe what percent of the total data changeability is explained by the admitted model (Table 2). In course of testing the significance of the regression coefficients, the F-Snedecor test was applied. The statistic program R was used for the computations. On the basis of the data the statistically relevant influence of the air temperature on the change of the share of the H_2SO_4 fraction in the sediment from the wastewater treatment plant in Bartkow and Barcza was shown as well as statistically significant influence of the air temperature on the change of the share of the NaOH fraction in the wastewater treatment plant in Radoszyce.

Table 2

The comparison of the results of the statistical analysis conducted for the excess sludge and subjected to temperature of the surroundings

Wastewater Treatment Plant / Fraction	Bartkow		Barcza		Radoszyce	
	R^2	p_{volume}	R^2	p_{volume}	R^2	p_{volume}
Ca-EDTA	0,79	0.110	0.64	0.203	0.27	0.470
Na-EDTA	0.72	0.151	0.88	0.063	0.85	0.076
H_2SO_4	**0.93**	0.038	**0.93**	0.036	0.20	0.548
NaOH	0.84	0.083	0.81	0.102	**0.96**	0.021

Together with the drop of the temperature, the phosphorus H_2SO_4 fraction shares in the case of the excess sludge from the mechanical-biological-chemical wastewater treatment plants (Fig. 6 and Fig. 7) and the shares of phosphorus NaOH fraction in the case of the sediment from the mechanical-biological wastewater treatment plant increase (Fig. 8).

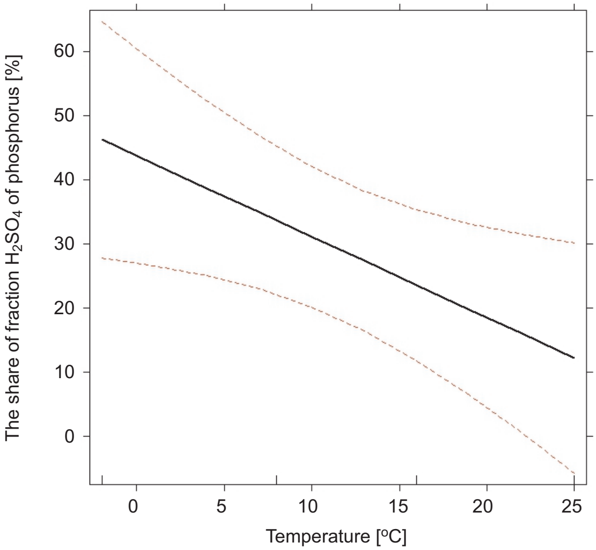

Fig. 6. Influence of the air temperature on the change of the share of the H_2SO_4 fraction of phosphorus in the sediment from the wastewater treatment plant in Bartkow

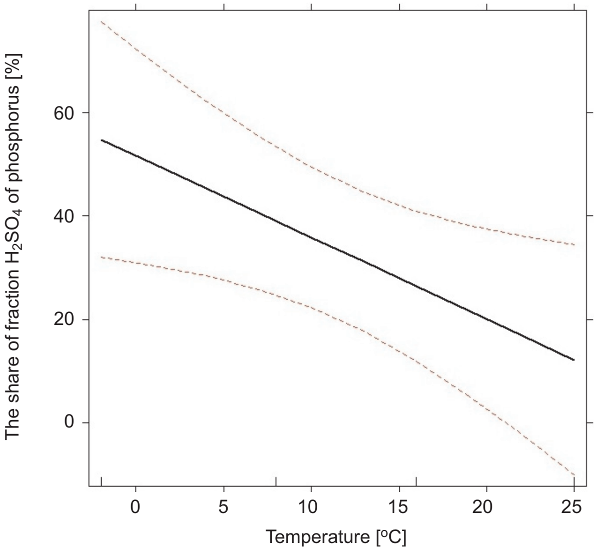

Fig. 7. Influence of the air temperature on the change of the share of the H_2SO_4 fraction of phosphorus in the sediment from the wastewater treatment plant in Barcza

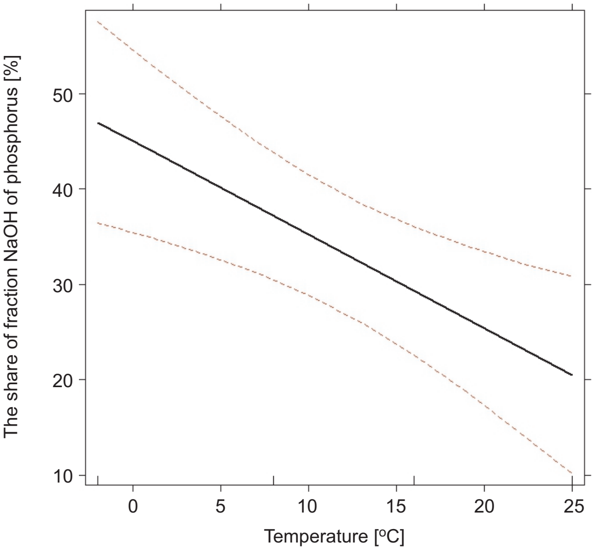

Fig. 8. Influence of the air temperature on the change of the share of the H_2SO_4 fraction of phosphorus in the sediment from the wastewater treatment plant in Radoszyce

Conclusions

The analysis of the research results allows to state that:

– The shares of the phosphorus forms in the excess sludge change in one-year cycle according to the climatic conditions (the temperature of the surrounding). The dominating phosphorus factions in the spring-summer period were the fractions containing the mobile phosphorus and the bioavailable phosphorus, that is fractions obtained after the extraction by means of chelating reagents in comparison to the fractions containing the organic phosphorus i.e. the forms not available for plants.

– According to the present technological conditions in the particular wastewater treatment plants, the examined excess sludges are characterized by opposite shares of the speciation forms of phosphorus. In the sediments from wastewater treatment plants with integrated mechanical-biological-chemical methods of wastewater treatment, it is easy to notice bigger differences between the shares of the phosphorus forms easily and not easily available for plants in one-year cycle than in the sediments from the mechanical-biological wastewater treatment plant

The knowledge of the quantitive shares of the mobile phosphorus fractions according to the type of the applied technology of the wastewater treatment and the assumption of the cyclic changes of the phosphorus fraction shares may influence the process of its retrieval from the wastewater sediments. Thanks to the speciation analysis of this element in the wastewater sediments, the amount of the contained bioavailable (in other words: mobile, susceptible to migration in the soil-water environment) phosphorus can be estimated.

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SPECJACJA FOSFORU W OSADACH ŚCIEKOWYCH Z WYBRANYCH OCZYSZCZALNI ŚCIEKÓW

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Abstrakt: Celem pracy było scharakteryzowanie osadów ściekowych pochodzących z różnych typów oczyszczalni ścieków komunalnych pod względem występowania form specjacyjnych fosforu. Przeprowadzono wstępną analizę specjacyjną z wykorzystaniem ekstrakcji sekwencyjnej według Goltermana. Polega ona na wykorzystaniu odczynników chelatowych (Ca-EDTA i Na-EDTA) oraz roztworów NaOH i H_2SO_4. Pomiar ilości fosforu odbył się metodą spektrofotometryczną zgodnie z obowiązującymi normami. Wykorzystując powyższą metodę, zbadano ilości poszczególnych frakcji fosforu w osadach ściekowych oraz stężenie fosforu ogólnego w ściekach oczyszczonych i surowych. Według Goltermana formą specjacyjną o największej dostępności dla organizmów żywych jest fosfor zaadsorbowany na powierzchni cząstek osadów, czyli tak zwany fosfor mobilny. Wstępne wyniki wskazują, iż znaczny udział fosforu mobilnego w osadach ściekowych występował w tych oczyszczalniach, gdzie stosowano zintegrowane metody oczyszczania ścieków (oczyszczalnie mechaniczno-biologiczno-chemiczne). Uzyskane rezultaty upoważniają do stwierdzenia, że w zależności od warunków fizyczno-chemicznych występujących w poszczególnych typach oczyszczalni ścieków, osady nadmierne charakteryzują się różnymi udziałami formy specjacyjnej fosforu mobilnego, co może wpływać na odzyskiwanie tego pierwiastka z osadów ściekowych.

Słowa kluczowe: fosfor mobilny, osady ściekowe, specjacja

DOI: 10.2428/ecea.2013.20(04)048 ECOL CHEM ENG A. 2013;20(4-5):515-523

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HEAVY METAL CONTENT OF SEWAGE SLUDGE IN THE WARMIAN-MAZURIAN PROVINCE

ZAWARTOŚĆ METALI CIĘŻKICH W OSADACH ŚCIEKOWYCH WOJEWÓDZTWA WARMIŃSKO-MAZURSKIEGO

Abstract: The work presents the results of physico-chemical studies on municipal sewage sludge from water treatment plants in the Warmian-Masurian province during the years 2005–2009. Dry mass and organic matter content and pH were determined in the samples. Heavy metals (cadmium, chromium, copper, nickel, lead, zinc, and mercury) were assessed by means of flame atomic absorption spectroscopy (FAAS) following mineralization in a microwave system. Dry matter content in the analyzed sewage sludge ranged from 18.1 % to 27.9 %, with the organic matter content in dry mass between 57.2 % and 69.9 %. Large differences in the average content of heavy metals were noted between the individual study years. Differences under 100 % were characteristic of Ni, Pb, Zn and Hg, and above 100 % of Cu, Cr and Cd. The differences between the minimal and maximal content ranged from 38 % to 205 % in relation to the average values in the study years. Among the analyzed microelements, Zn and Cu (included in the group of microelements applied in agriculture) were most prevalent The remaining heavy metals occurred in amounts lower than those specified by the acceptable norms for application in agriculture.

Keywords: sewage sludge, organic mater, heavy metals

The increasing production of sewage waste necessitates finding a method that would allow for its ecological utilization. Among those available, its application in environmental engineering is the most significant and economically justified, which has been confirmed by numerous publications [1–7]. This is because sewage sludge constitutes a rich source of organic matter and contains all the nutrients essential to plants [1, 2, 8–11]. It is municipal or municipal-industrial origin dictates a need to conduct chemical analysis for the content of fertilizing substances as well as heavy metals, since their environmental application in the raw or treated state depends on heavy metal content

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[12]. Toxic metals may be mobilised in the soil and be taken up by plants or transported in ground waters [13–15].

The heavy metal content of domestic sewage does not usually exceed the permissible norms, however the addition of industrial sewage can disqualify sewage sludge from land application. Moreover, sewage sludge is a substrate for humification and can therefore replace natural fertilizers on stockless farms [16–18].

The work describes the heavy metal content of sewage sludge in the Warmian-Masurian province in the years 2005–2009.

Materials and methods

Samples of municipal sewage sludge from the Warmian-Masurian province (NE Poland) were analyzed in: 2005 (47 samples), 2006 (43 samples), 2007 (47 samples), 2008 (20 samples) and 2009 (23 samples) at the Regional Chemical and Agricultural Station in Olsztyn. Sludge samples, collected in accordance with PN-EN ISO 5667-13:2004 and PN-ISO 5667-15:2004, were assayed for dry matter content – by the gravimetric method, pH – by the conductometric method, and organic matter content – based on loss-on-ignition in a muffle furnace at 550 ^{o}C. The concentrations of heavy metals (cadmium, chromium, copper, nickel, lead, zinc and mercury) were determined by flame atomic absorption spectroscopy (FAAS) after microwave mineralization in a mixture of concentrated nitric(V) and chloric(VII) acids.

Results and discussion

The numerical data illustrating the dry matter and organic matter content as well as pH of sewage sludge in the years 2005–2009 has been presented in Table 1. The dry mass content of the analyzed municipal sewage sludge ranged from 18.1 % to 27.9 %.

Table 1

The content of dry matter and organic matter and value pH in sewage sludge in the Warmian-Masurian province

Parameter	Years					Mean 2005–2009
	2005	2006	2007	2008	2009	
Dry matter	27.6	27.9	24.7	18.1	23.2	24.3
Organic matter [% d.m.]	59.4	58.8	66.4	69.9	57.2	62.3
pH in H_2O	7.8	7.6	7.5	7.3	7.5	7.5

Similar parameters (18.4–25.5 % d.m.) were found in sewage sludge from the Water Treatment Plant in Suwalki in 2010 [1] as well as in sewage sludge obtained in the years 2002–2003 from three Spanish water treatment plants (21.9–25.8 % d.m.) [19]. Higher variability in dry mass content (16.0–50.8 %) was noted by Bauman-Kaszubska and Sikorski [2] who, in 2005, analyzed 10 average-sized and large water treatment plants in the Mazowieckie and Swietokrzyskie province. In municipal sewage sludge from the Dolnoslaskie province, Spiak and Kulczycki [20] recorded an average dry mass of 20.7 %, which oscillations in the range of 1.8 % to 44.2 %. Kalembasa et al [21] determined the changes in the average dry matter content of sewage sludge from selected water treatment plants in the region of Siedlce to be anywhere from 8.2 % to 45.3 %. Such high variability is the result of different technologies used for drying sewage sludge. The average water content, equal to approximately 75 %, is similar to the water content of manure. This makes it possible to apply fresh sludge in agriculture.

The content of organic matter in the dry mass of the analyzed sewage sludge ranged from 57.2 to 69.9 % (62.3 % on average). This signifies a high humus value of the analyzed sludge [2, 3, 22]. Similar results were obtained by Kazanowska and Szacilo [1] as well as Galvin et al [19], whose studies revealed dry matter contents ranging from 62.7–72.0 % and 58.7–73.9 %, respectively. Gambus and Wieczorek [11], when assessing the fertilizing value of sewage sludge from the water treatment plants in Krzeszowice and Niepolomice, determined respective organic matter contents of 40 % and 54 %. These values are close the national average [23].

An important physicochemical property of sewage sludge is its pH value. The analyzed sewage sludge mass was characterized by a slightly basic pH value (over 7) and thus, does not lead to soil acidification. In the studies of other authors, pH values ranged from 5.8 to 9.7 [2] and 6.4 to 7.9 [1]. Sewage sludge from four water treatment plants in southeastern Poland analyzed by Oleszczuk [9] were characterized by a slightly acidic pH (6.1–6.9). Spiak and Kulczycki [20] noted pH values ranging from 5.1 to 8.4 (6.7 on average) in sewage sludge taken from 9 water treatment plants located in southwestern Poland. Skorbilowicz [24], on the other hand, noted primarily acid values of pH (5.0–7.1) in sewage sludge from the Podlaskie province.

The analysis of heavy metal content in sewage sludge is illustrated by the numerical data presented in Table 2.

Table 2

Average content of trace elements in municipal sewage sludge over the experimental period

Year	[mg · kg^{-1} d.m.]						
	Cd	Cr	Cu	Ni	Pb	Zn	Hg
2005	3.57	26.0	131.4	37.8	38.7	675.0	0.700
2006	2.47	33.7	102.5	30.2	30.0	648.2	0.646
2007	2.38	24.2	119.1	48.9	41.4	611.1	0.650
2008	1.06	52.4	201.9	49.3	43.3	966.9	0.810
2009	0.74	64.7	217.0	32.8	38.2	954.8	0.708
Mean	2.04	40.2	154.4	39.8	38.3	771.2	0.703
SD	1.20	12.6	33.6	6.0	3.6	118.9	0.04
CV [%]	58.7	32.1	21.8	15.3	9.5	15.3	6.3

SD – standard deviation, CV – coefficient of variation.

From the data contained in the table it can be observed that over the course of 5 years covered by the studies, fairly significant quantitative changes occurred in the analyzed microelements. The highest content of Cd was recorded in the year 2005, Cr and Cu in the year 2009, and Ni, Pb, Zn, and Hg in 2008. Sewage sludge produced in 2007 contained the least Cr and Zn, in the year 2006 – Cu, Ni, Pb and Hg, and in 2009 – Cd.

Among the analyzed microelements, Zn and Cu (elements included in the group of microelements applied in agriculture) were the most prevalent. The remaining heavy metals occurred in quantities lower than the permissible norms for their application in agriculture [12].

The average percentage content of individual heavy metals in the total sum varies greatly, from 0.07 % (Hg) to 73.68 % (Zn). In decreasing order, the content of heavy metals is as follows:

$$\mathrm{Zn} > \mathrm{Cu} > \mathrm{Cr} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Cd} > \mathrm{Hg}$$

Heavy metals which are considered to be micronutrients, *ie* Zn and Cu, make up 88.44 % of all analyzed microelements.

The ranges of values for the analyzed metals in sewage sludge from the Mazurskie province as well as the results of studies on metals from Polish municipal water treatment plants carried out by other authors have been presented in Table 3.

The content of cadmium, the element characterized by the highest variability in terms of concentration in the collected sewage sludge, oscillated in the range of 0.72–4.60 $\mathrm{mg \cdot kg^{-1}}$ d.m. These values are low when compared to other water treatment plants in Poland. Lower values of cadmium were reported by Skorbilowcz [24] in the sewage sludge of three water treatment plants in the Podlaskie province. Sewage sludge from Wielkopolska [25] and Andrychowo [26] contained more Cd.

The next analyzed metal was chrome, with concentrations ranging from 68 to 91 $\mathrm{mg \cdot kg^{-1}}$ d.m. Only in the case of sewage sludge from the water treatment plant in Suwalki [1] and Lubartowo [27] did the value of this element not exceed 100 $\mathrm{mg \cdot kg^{-1}}$ d.m. Sewage sludge from water treatment plants in the vicinity of Poznan contained very high amounts of Cr were in the [25].

Copper is among the microelements that are essential to plants. Its content was found to be from 37.8–362.2 $\mathrm{mg \cdot kg^{-1}}$ d.m. Sewage sludge from water treatment plants in southwestern Poland [9] and Katy Wroclawskie [28] was characterized by similar maximum copper contents. The most Cu (similarly to Cr, Ni and Pb) was noted by Czekala and Jakubus [25] in sewage sludge from Wielkopolska. This signifies a high share of industrial wastewater in the sewage.

The content of nickel in the collected sewage sludge oscillated in the range of 9.5–65.0 $\mathrm{mg \cdot kg^{-1}}$ d.m. These values are average in relation to the content of this element in the sewage sludge of other water treatment plants. The lowest amount of nickel, equal to only 14.0–19.0 $\mathrm{mg \cdot kg^{-1}}$ d.m., was determined by Kazanowska and Szacilo [1] in sewage sludge from the water treatment plant in Suwalki.

The amount of lead in the analyzed sewage sludge ranged from 15.6 to 73.4 $\mathrm{mg \cdot kg^{-1}}$ d.m. These values are typical of sewage sludge from water treatment plants with a low share of industrial wastewater. Grzywnowicz and Strutynski [26] indicated

Table 3

The concentration of heavy metals (range of values) in sewage sludge samples from water treatment plants in the Warmian-Masurian province and a comparison of heavy metal contents with data in literature (in Poland)

Water treatment plants	[mg · kg^{-1} d.m.]							References
	Cd	Cr	Cu	Ni	Pb	Zn	Hg	
Suwalki	1.8–8.9	14.2–23.0	110–128	14.0–19.0	15.6–19.0	1020–1072	0.72–0.76	[1]
Mazowieckie Swietokrzyskie	0.4–8.0	0.5–203.0	13–280	7.8–82.4	24.0–105.0	0.8–6700.0	0.1–5.9	[2]
Podkarpackie	1.9–7.9	27.6–120.0	156.0–335.0	21.7–155.0	37.5–59.5	1015–1385	a	[9]
Podlaskie	0.0–1.5	20–290	20–112	6.8–31.9	0.2–13.0	402–3240	a	[24]
Wielkopolskie	4.8–29	32.6–666	128–970	34–225	25–161	1077–3249	0.85–2.60	[25]
Andrychow	5.60–11.45	98–203	170–564	99–225	149–268	2020–3669	a	[26]
Lubartow	2.9–7.98	19.2–99.6	48.2–66.3	21.0–43.4	33.1–95.0	232.0–574.0	0.00–0.76	[27]
Katy Wroclawskie	3.4–7.3	68–91	281–332	34–45	23–34	1035–1140	0.67–0.96	[28]
Warmian-Masurian	0.72–4.60	16.9–97.8	37.8–363.2	9.5–65.0	15.6–73.4	553.1–1243.0	0.70–1.20	This study

a – data is not available.

Table 4

The concentration of heavy metals in sewage sludge samples from water treatment plants in the EU (data from literature)

Water treatment plants	[mg · kg^{-1} d.m.]							References
	Cd	Cr	Cu	Ni	Pb	Zn	Hg	
Spain	1.10–18.3	38–3809	146–337	17.80	43.4–251	458–1951	a	[14]
Denmark	0.5–16	8–108	75–515	8–141	11–420	215–1610	0.3–7.0	[29]
Greece	10	370	1200	300	330	4500	a	[30]
Slovenia	1.5–4.22	408–1235	185–695	372–995	88–175	1025–2650	a	[31]
Germany	3.2–21	80–630	370–384	38–131	158–290	1300–2140	2.4–4.8	[32]
Lithuanian	0.34–7.83	21–656	14.5–426	7.6–69.8	4.8–475	71–1698	0.1–1.475	[33]

a – data is not available.

a high concentration of Pb, up to 268 mg · kg^{-1} d.m., in sewage sludge collected from the water treatment plant in Andrychowo.

Zinc is an important element that can be found in sewage sludge. Similarly to copper, this microelement is essential to plants, but its excessive concentration in soil can be harmful. Zinc content oscillated in the range of 533.1 to 1243.0 mg · kg^{-1} d.m. Amounts similar to the high range value of this microelement were noted by Kazanowska and Szacilo [1], Oleszczuk [9] and Krutysz-Hus and Chmura [28]. Very high quantities of this metal, reaching levels of 6700.0 mg · kg^{-1} d.m., were reported in the work of Bauman-Kaszubska and Sikorski [2].

The metal that occurs in the lowest qualities in sewage sludge is mercury. During the study period, its content ranged from 0.700 to 1.20 mg · kg^{-1} d.m. The lowest quantities of this microelement (0.72–0.76 mg · kg^{-1}) were noted by Kazanowska and Szacilo [1] in their studies of sewage sludge from the water treatment plant in Suwalki, whereas the highest (up to 5.9 mg · kg^{-1} d.m.) values were determined by Bauman-Kaszubska and Sikorski [2] in their analysis of sewage sludge from the Mazowieckie and Swietokrzyskie province.

Table 4 presents the results of the analysis of municipal sewage sludge in a few European Union countries. The concentrations of heavy metals in sewage sludge are similar to results obtained in the Warminsko-Mazurskie province and other regions of Poland. Higher upper range values of heavy metal contents may be caused by the high changeability of the chemical composition of municipal wastewater resulting from the addition of industrial wastewater.

Conclusions

The conducted studies regarding the value of sewage sludge produced in the Warmian-Masurian province during the years 2005–2009 revealed sludge to be a substance that can be applied in agriculture in its raw state or upon being processed into compost. It contains over 24 % dry mass and over 62 % organic matter and thus is a rich substrate for the production of humus. The heavy metal content, although different in the individual years, falls within the acceptable norms. A higher zinc and copper content in relation to the remaining microelements is beneficial for the production of plant biomass.

The obtained results lead to the following conclusions:

1. The sum of the six analyzed heavy metals averaged 1047 mg · kg^{-1} d.m., with a large difference in the individual components (from 0.703 mg · kg^{-1} Hg to 771.2 mg · kg^{-1} d.m. Zn).
2. Significant quantitative changes were observed between the study years, the smallest in 2005 and largest in 2008.
3. Cadmium and Mercury were found to be characterized by, respectively, the highest and lowest variability in terms of their concentration in the analyzed sewage sludge.
4. When applied in agriculture, the analyzed sewage sludge is a sufficient source of zinc and copper for cultivated plants.

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ZAWARTOŚĆ METALI CIĘŻKICH W OSADACH ŚCIEKOWYCH WOJEWÓDZTWA WARMIŃSKO-MAZURSKIEGO

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Abstrakt: W pracy podano wyniki fizykochemicznych badań komunalnych osadów ściekowych z oczyszczalni ścieków województwa warmińsko-mazurskiego w latach 2005–2009. W próbkach osadów oznaczono zawartość suchej masy, pH i zawartość materii organicznej. Metale ciężkie (kadm, chrom, miedź, nikiel, ołów, cynk i rtęć) oznaczono metodą płomieniowej absorpcyjnej spektroskopii atomowej po wcześniejszej mineralizacji w systemie mikrofalowym. Zawartość suchej masy w badanych komunalnych osadach ściekowych wynosiła od 18,1 do 27,9 %, a zawartość materii organicznej w suchej masie wynosiła od 57,2 do 69,9 %. Stwierdzono duże różnice w średniej zawartości metali ciężkich między latami badań. Różnice poniżej 100 % dotyczą Ni, Pb, Zn i Hg, natomiast powyżej 100 % Cu, Cr i Cd. Natomiast wahania między minimalną a maksymalną zawartością zawierają się w granicach od 38 do 205 % w stosunku do wartości średnich w latach badań. Spośród badanych mikroskładników najwięcej przypadało na Zn i Cu (pierwiastki zaliczane do mikroelementów stosowanych w rolnictwie). Pozostałe metale ciężkie występowały w ilości mniejszej niż określają normy dopuszczalne ich stosowania w rolnictwie.

Słowa kluczowe: osady ściekowe, materia organiczna, metale ciężkie

DOI: 10.2428/ecea.2013.20(04)049 ECOL CHEM ENG A. 2013;20(4-5):525-533

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DEGRADATION OF *n*-ALKANES IN OIL POLLUTED SOIL AFTER STIMULATION BY FYRE-ZYME ENZYME PREPARATION AND HYDROGEN PEROXIDE

ROZKŁAD *n*-ALKANÓW W ZAOLEJONEJ GLEBIE PO STYMULACJI PREPARATEM ENZYMATYCZNYM FYRE-ZYME I NADTLENKIEM WODORU

Abstract: Petroleum substances are widely used in many industries and are used as lubricants and fuels in motor vehicles. Due to the pipeline failure, lost of substances on the loading stations area and traffic crashes, petroleum contamination of soils are very common. High concentration of petroleum pollutants in the soil, leads to reduced activity of the indigenous microflora and extends their fate in the environment. However solubility in water of petroleum products is low, contamination could easily move from accident site to other places with surface and groundwater streams. It is especially important on water resources or agriculture areas. The high costs of removal of oil spills to the soil and ground, forces to search for low-cost and effective methods of soils decontamination by "in situ" methods. The aim of this study was to compare the effectiveness of biodegradation of diesel fuel and mineral oil in the soil contaminated with petroleum substances, after "Fyre-Zyme" enzyme reagent stimulation and / or hydrogen peroxide. Obtained results indicate on stimulation of degradation process of diesel fuel and mineral oil, either by used enzyme and hydrogen peroxide compared with the control samples in 60 days period of experiment. This indicates the possibility of use of tested additives for soils bioremediation processes as a cheap alternative for ex-situ methods.

Keywords: oil, bioremediation, soil, enzymes, hydrogen peroxide

Introduction

Petroleum substances are widely used in many industries and are used as lubricants and fuels in motor vehicles. Special care of transport containers is essential in order to

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limit the detrimental effects of diesel oil, mazout or petrol leakages to the natural environment. Nevertheless, these leakages still occur as a result of land or sea transport catastrophes or damaging transmission routes, causing water degradation and preventing arable lands from producing [1]. To absorb these petroleum by-products sorbents are commonly used. However, in spite of their multiple merits, mineral and organic sorbents have a few notable drawbacks: their production usually requires considerable expense in order to obtain natural rock sources and other organic material [2]. Moreover, used mineral and organic sorbents are hazardous waste and, therefore, in accordance with actual law regulations must be converted thermally or deposited in the special landfill for hazardous waste. Due to the significant pipeline failure, lost of high loads of substances on the loading stations area and traffic crashes, when sorbents were not used, the petroleum contamination of soils are very common. High concentration of petroleum pollutants in the soil, leads to reduced activity of the indigenous microflora and extends their fate in the environment [3, 4]. In case of low amount of hydrocarbons contamination, it is possible use of compost and lime for improve natural degradation processes and plants growth conditions [5]. But high load of diesel fuel or lubricants lead to very long time of natural bioremediation, as an effect of the significant decrease of the colony forming units [6]. The high costs of removal of oil spills to the soil and ground, forces to search for low-cost and effective methods of soils decontamination by "in situ" methods [7]. In order to elimination of organic compounds (mostly hydrocarbons but also alcohols) present in soil, are widely used microbiological purification, oxygenation, phytoremediation of contaminated soils or rinsing with detergents [8–13]. Remediation processes are dependent on many factors where climate conditions play a crucial role [14].

The aim of this study was to compare the effectiveness of biodegradation of diesel fuel and mineral oil in the heavily contaminated with petroleum substances soil, after stimulation of Fyre-Zyme enzyme preparation and / or hydrogen peroxide.

Material and methods

Soil samples for experimental purposes were collected from hard contaminated area after long-term contamination with different petroleum products. Determination of the degree of degradation of diesel fuel and mineral oil in contaminated soil was conducted in the laboratory conditions by use:

– Fyre-Zyme enzyme preparation (S + FZ);
– hydrogen peroxide (S + H);
– Fyre-Zyme enzyme preparation and hydrogen peroxide (S + FZ + H).

Each experimental pot was fed by 1 kg of contaminated soil, and then the Fyre-Zyme enzyme preparation was added in an amount of 10 % (m/m). Hydrogen peroxide was added in an amount of 0.5 gO_2/dm^3. Control samples (S) without the addition were incubated. Humidity was maintained at 60 % and at 2 days periods weight loss of water was replenished. The prepared soil in pots were incubated at room temperature 22 ^oC (± 2 ^oC). The duration of the experiment was 60 days. Pot experiments established in 3 replications. The kinetics of the chemical changes were monitored by taking 1 g soil samples from each objects, and then averaged and at 0, 30 and 60 days was determined changes in the concentration of oil products (diesel fuel and mineral oil) in the soil. Also only aliphatic hydrocarbons with carbon chain from C8 to C40, were determined. These compounds were divided on two groups (C8–C21 and C22–C40) connected to boiling temperatures characteristic for diesel and mineral oil (126–343 and 344–522 respectively).

All soil samples were extracted for 6 hours in fexIKA® automatic extractor after drying with anhydrous sodium sulphate (POCH). Mixture of hexane and dichloromethane (9/1 v/v) was use for extraction. After extraction sampes were dried, evaporated and stored in amber glass vials for analysis. Aliphatic hydrocarbons, diesel fuel and mineral oil were determined by GC-FID method on apparatus Varian CP-3800 with Varian capillary column VF1-ms (30 m × 0.53 mm × 1.50 μm). For analysis purposes, the chromatograph injector heated to 305 ^{o}C, and the FID detector to 325 ^{o}C. GC oven temperature program was started at 100 ^{o}C hold for 1 minute, then heated to 320 ^{o}C at a rate of 12 ^{o}C per minute, and keeping it at the end of the analysis for 12 min. During all tests the flow of carrier gas (He), through the column was 3 cm^3 per minute. Calibration curves were made on the basis of standard RGO 610 and RGO 722 ® from LGC Promochem and 31630 from Restek ® company. The presented results are the mean of 3 replicates. Diesel fuel and mineral oil were calculated as summary peaks of all detected organic compounds in specific boiling temperature ranges: 126–369 ^{o}C for diesel and 372–522 ^{o}C for the motor oil.

Results and discussion

In this work was conducted a purification process of a mixture of soil and mineral oil with different pacing techniques (S + H, S + FZ, FZ + S + H) in 60 days' time period. These samples were analyzed in parallel for changes of the content of aliphatic hydrocarbons in diesel and mineral oil to identify trends (directions) of the degradation. To demonstrate the effectiveness of the stimulation technique (degradation processes), in this paper shows the relative changes in the concentrations of individual hydrocarbons in relation to the control sample – (S), *ie* soil without additions, in which the processes take place only with the involvement of autochthonic microorganisms.

However, hard polluted soil used in experiment, which contain 66.07 g/kg d.m. of petroleum products, is not a good environment for natural bioremediation process, obtained results indicate on stimulation effect of used additions on petroleum products decomposition in investigated soil. In the first group (diesel range) an increase of amounts of analyzed hydrocarbons was observed (Fig. 1–3). On the other hand, in case of object S + FZ this phenomenon was noted only for C8, C13 and C14 after 30 days, and additionally for C9, C10, C15 and C16 on the end of experiment (Fig. 1). In fact of high contents of C8 and C14 mean value of degradation process speed (in comparison with control sample) was positive (0.97 %) after 30 days and 4.11 % after 60 days. In the experimental pots S + FZ + H these values were higher: 49.6 and 15.9 % respectively for 30 and 60 days. Diesel fuel concentration was different in case of hydrogen peroxide use – in S + H group. In the halftime mean value was almost twice higher than in control (90.2 %), but after 60 days a slight decrease (–12.3 %) was observed. The highest affectivity was noted for C11 (–58.4 %). Rise of hydrocarbons content in experimental series in comparison with natural degradation process in control samples is noted as natural phenomenon in effect of long-chain aliphatic compounds degradation (bio-cracking). So, in experimental series the most effective process was

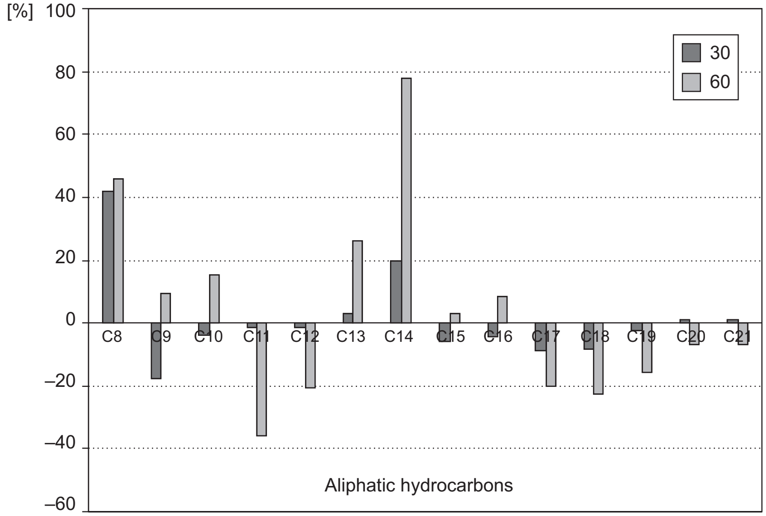

Fig. 1. Relative changes of aliphatic hydrocarbons (diesel range) content in object S + FZ in comparison with control additive-free sample (S) after 30 and 60 days of incubation

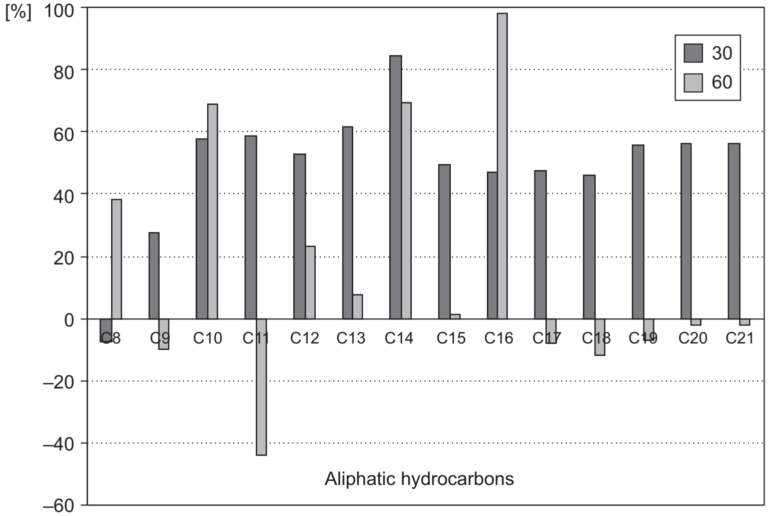

Fig. 2. Relative changes of aliphatic hydrocarbons (diesel range) content in object S + FZ + H in comparison with control additive-free sample (S) after 30 and 60 days of incubation

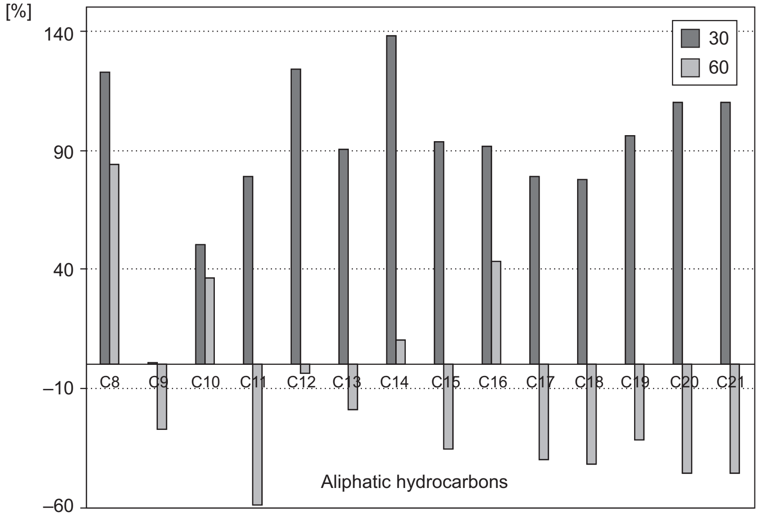

Fig. 3. Relative changes of aliphatic hydrocarbons (diesel range) content in object S + H in comparison with control additive-free sample (S) after 30 and 60 days of incubation

observed in S + FZ objects. The most sensitive compound (from diesel range hydrocarbons) in all testes series was undecane (C11) with values from –35.7 to –58.4 % in comparison with control.

Long-chain hydrocarbons (mineral oil range) degradation had different characteristic than diesel. In S + FZ objects (Fig. 4) during first 30 days, all tested compounds (C22–C40) were degraded in 38.7 % (mean value). In second part of experiment mostly

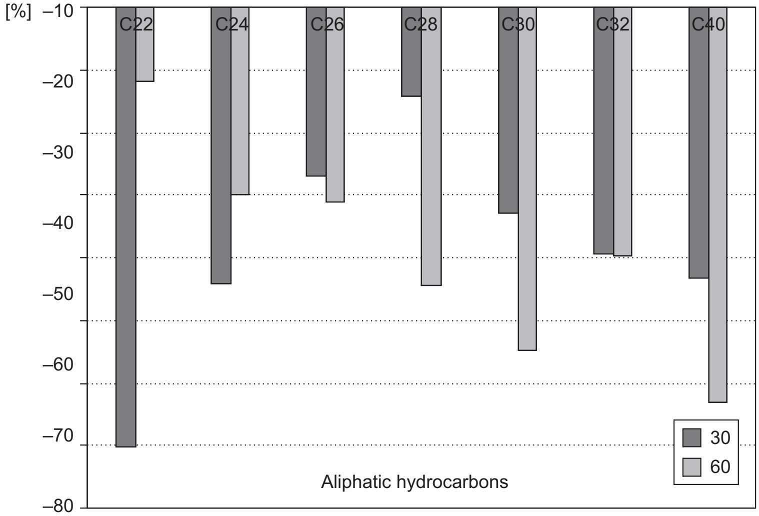

Fig. 4. Relative changes of aliphatic hydrocarbons (mineral oil range) content in object S + FZ in comparison with control additive-free sample (S) after 30 and 60 days of incubation

was degraded long-chain hydrocarbons (C28–C40), however in first 30 days the most effective process was noted for C22, C24 and C40.

In series S + FZ + H pots (Fig. 5), process of decomposition had similar profile like in case of S + FZ objects. After 30 days the most degraded compounds were also C22, C24, C40, but in case of C26 and C28 degradation was slower than in control what was not present in S + FZ objects. In effect mean value of degradation speed was only

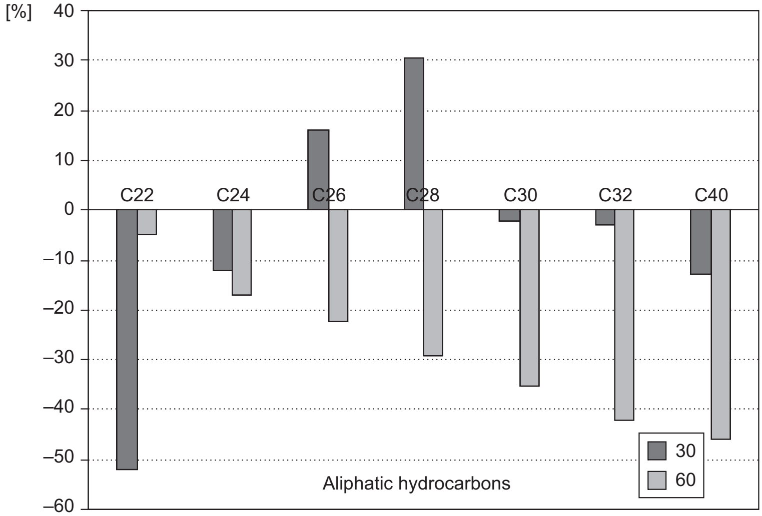

Fig. 5. Relative changes of aliphatic hydrocarbons (mineral oil range) content in object S + FZ + H in comparison with control additive-free sample (S) after 30 and 60 days of incubation

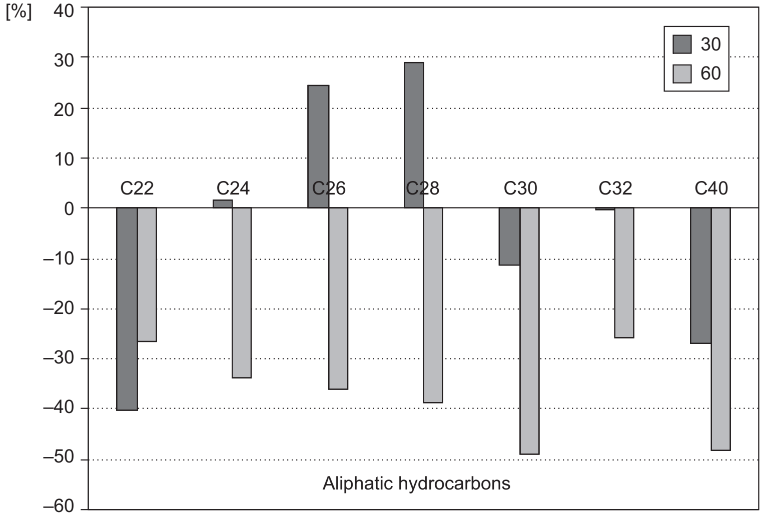

Fig. 6. Relative changes of aliphatic hydrocarbons (mineral oil range) content in object S + H in comparison with control additive-free sample (S) after 30 and 60 days of incubation

–5.1 %. On the end of experiment the highest decomposition efficiency was noted for C28–C40, and mean value was better than in control (–28.2 %). In objects with hydrogen peroxide addition (S + H), decomposition was similar than in S + FZ + H objects (Fig. 6). In first part of experiment only two compounds (C22 and C40) were effective degraded, but for *n*-alkanes C24–C28 in comparison to control samples, worst results were noted. In effect mean decomposition process was slightly better than in control but low (–3.3 %). In second part, process was faster (like in case of S + H diesel range hydrocarbons) and total effectiveness (–36.8 %) was close to noted in S+FZ objects.

Degradation of *n*-alkanes was different in all tested samples. In case of "diesel range" compounds, the best results (54.0 % of biodegradation) was obtained in sample with hydrogen peroxide addition (similar to total diesel fuel content). Worst results for these compounds (only 18.1 %) was observed in samples with enzyme preparation. In case of "long-chain" *n*-alkanes (C22–C40), the highest degradation intensity (46.5 %) was observed in samples with Fyre-Zyme enzyme preparation. Similar to diesel fuel in samples with Fyre-Zyme preparation and H_2O_2 addition and only with hydrogen peroxide was observed good results (41.2 and 40.3 % respectively). Better results (degradation 89–92 % in 112 days) were noted in experiment on light and heavy soils modified with compost or bentonite and specific microflora consortium, however diesel fuel concentration was 10 times lower than in this work [4]. So it is possible to choose precisely an optimal method in case of pollution type.

Obtained results from experiments conducted with composts as a matrix and motor oil degradation intensity were different than noted in this work. Intensity of decomposition after 60 days was high (62.9–76.4 %).

However oil content was high but experimental composts containers were well vented, and composts were prepared 6 months before this experiment by diesel oil spreading for microbial consortium adaptation. Additionally organic pollution was mixed with composts 1 hour before experiment. Results obtained in this work show that in case of high contamination by petroleum products (above 10 g/kg d.m. of soil), it is necessary to increase degradation speed with enzyme preparation or hydrogen peroxide additions [6].

Conclusion

Petroleum products in soil lead to multidirectional long-time degradation polluted areas. A quick and cheap methods of ground reclamation are the most wanted to introduce in practice. Use of different sorbents is expensive because used sorbents have to be incinerated or deposited in the special landfill for hazardous waste. Moreover in many accidents it is too late for sorption process. Obtained results indicate on stimulation of natural degradation process of diesel fuel and mineral oil in heavily contaminated soil. The best results was obtained either for samples with Fyre-Zyme enzyme preparation (in case of motor oil range *n*-alkanes) or hydrogen peroxide (in case of diesel oil range *n*-alkanes) compared with the control samples in 60 days period. Used mixture of FZ enzyme preparation and hydrogen peroxide also was effective but especially for heavy compounds (*eg* mineral oil fraction). This indicates the possibility of use of tested additives for environmentally friendly, highly effective soil bioremediation processes. Moreover this "in-situ" method is cost-effective, what could be a reason for wide use in many cases.

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ROZKŁAD *n*-ALKANÓW W ZAOLEJONEJ GLEBIE PO STYMULACJI PREPARATEM ENZYMATYCZNYM FYRE-ZYME I NADTLENKIEM WODORU

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Abstract: Substancje ropopochodne znajdują szerokie zastosowanie w wielu gałęziach przemysłu, a także są stosowane jako środki smarne i pędne w pojazdach mechanicznych. Z uwagi na awarie sieci przesyłowych, obrót tymi substancjami na stacjach przeładunkowych, a także katastrofy w ruchu lądowym, zanieczyszczenia ropopochodne gleb są częstym zjawiskiem. Duża koncentracja zanieczyszczeń naftopochodnych w glebie prowadzi do zmniejszenia aktywności mikroflory autochtonicznej i poprzez ograniczenie dopływu tlenu do profilu glebowego, wydłuża czas ich zalegania w środowisku. Wysokie koszty likwidacji skutków wycieków ropopochodnych do gleb i gruntu zmuszają do poszukiwania tanich i efektywnych metod usuwania zanieczyszczeń metodami „in situ". Celem niniejszej pracy było porównanie efektywności biodegradacji *n*-alkanów rozpatrywanych w podziale na 2 grupy: oleju napędowego oraz oleju silnikowego w glebie silnie zanieczyszczonej substancjami ropopochodnymi, po stymulacji preparatem enzymatycznym Fyre-Zyme lub/i nadtlenkiem wodoru. Uzyskane wyniki wskazują na stymulowanie rozkładu oleju napędowego oraz silnikowego zarówno poprzez zastosowany preparat enzymatyczny (który najwyższą efektywność wykazywał w przypadku węglowodorów o długości łańcucha węglowego C22–C40), jak i nadtlenek wodoru (najbardziej efektywny do stymulacji rozkładu węglowodorów C8–C21) w porównaniu do grupy kontrolnej w okresie 60 dni. Wskazuje to na potencjalne możliwości zastosowania badanych dodatków do przyspieszania procesu bioremediacji gleb.

Słowa kluczowe: ropopochodne, bioremediacja, gleba, enzymy, nadtlenek wodoru

DOI: 10.2428/ecea.2013.20(04)050 ECOL CHEM ENG A. 2013;20(4-5):535-544

Krzysztof GONDEK[1]

EFFECT OF SOIL POLLUTION WITH PAHs ON THE AMOUNT OF MAIZE BIOMASS AND ACCUMULATION OF CADMIUM AND LEAD

WPŁYW ZANIECZYSZCZENIA GLEBY WWA NA ILOŚĆ BIOMASY KUKURYDZY ORAZ AKUMULACJĘ KADMU I OŁOWIU

Abstract: Trace element bioavailability is of key importance for stimulation or inhibition of plant growth and development processes at later stages of their life and in result leads to changes of biomass biological value, *eg* limiting its use. As assessment of artificial soil pollution with benzo(a)pyrene, chrysene and fluorene effect on the quantities of biomass and accumulation in it of cadmium and lead was conducted as a pot experiment. The soil pollution with the studied aromatic hydrocarbons did not inhibit growth or development of maize shoots and roots. The greatest amount of biomass was obtained in the object where the soil revealed an elevated contents of the analyzed aromatic hydrocarbons. Value of tolerance index in the objects where the stress agent was introduced was above one, which indicates the absence of soil pollution with benzo(a)pyrene, chrysene and fluorene effect on plant biomass quantity. Value of tolerance index below one concerned only biomass from the control object. Significant increase in Cd content and its quantities taken up by maize shoots was registered on the treatments where dichloromethane and polycyclic aromatic hydrocarbons were added to the soil in comparison with the unpolluted objects. The content and amounts of absorbed lead were the lowest on the object where the soil was the most polluted. Values of maize shoot biomass Cd pollution index were apparently higher in the objects where the soil was contaminated with polycyclic aromatic hydrocarbons in comparison with the values obtained in the object where soil received only mineral nutrient solution. Values of translocation index do not point to cadmium accumulation in plant shoots. Both the values of pollution index and translocation index for lead in the objects with elevated PAHs content in soil and in the object where the soil was contaminated with these substances were below one, which did not confirm excessive lead accumulation in maize shoots.

Keywords: soil, pollution, polycyclic aromatic hydrocarbons, cadmium, lead

Introduction

Polycyclic aromatic hydrocarbons and heavy metals are the factors which most frequently cause chemical pollution of soil [1–4]. The main sources of chemical soil

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pollution are industry, agriculture and transport [5]. Depending on the pollutant emission, the rate of soil degradation may be different, conditioned also by its kind, which is connected with buffering properties and functioning of natural self-cleaning mechanisms in soil [6].

Soil pollution affects changes of not only its chemical properties but also alters quantitative and qualitative composition of soil microflora. Quantitative and qualitative changes of soil microflora directly influence a majority of biochemical processes occurring in the soil environment, which beside the processes of pollutant substances degradation, concerns also processes accompanying transformations of macroelements and trace elements [7]. In case of oil derivative pollutants a problem of unfavourable physical soil properties appears, which results in worsening of water-air relationships.

The outcome of these changes is worsening of plant living conditions, which affects the obtained crop yield and its quality. The quality of crops is of key importance regarding its destination. Anti-nutritional substances load in biomass results in its limited use. Toxic trace elements, such as cadmium or lead contained in the polluted soil may easily accumulate in plants. The content of these elements in plants requires monitoring because their potentially dangerous levels (without the symptoms of harmful effect on plants) may be reached in diets of both animals and people [8, 9].

The research was conducted to assess the effect of artificial soil pollution with polycyclic aromatic hydrocarbons on the amount of produced maize biomass and its accumulation of cadmium and lead.

Material and methods

The investigations were conducted in 2009–2010 as a pot experiment on soil material collected from Ap (0–20 cm) layer of an arable field.

The experimental soil was polluted with three hydrocarbons from PAH group: benzo(a)pyrene, chrysene and fluorene with diversified physicochemical properties. Because of the fact that the soil environment is never polluted with single compounds of this group, their mixtures were used for the experiment [10–12]. Benzo(a)pyrene (BaP), chrysene (Ch) and fluorene (Fl) were added to the soil as liquids dosed 0.1 $\text{mg} \cdot \text{kg}^{-1}$ d.m. of each substance and 10 $\text{mg} \cdot \text{kg}^{-1}$ d.m. of each substance. An appropriate amount of PAHs was dissolved in dichloromethane. The experiments comprised: the control (K) – soil with natural concentrations of studied PAHs and without mineral salt supplement; object (0) – soil with natural concentrations of studied PAHs and mineral salt supplement, object (I) – soil with dichloromethane and mineral salts supplement, object (II) – soil with a supplement of 0.3 $\text{mg} \cdot \text{kg}^{-1}$ of soil d.m. PAHs (0.1 mg BaP + 0.1 mg Ch + 0.1 mg Fl) + mineral salts – the amount of PAHs introduced to the soil on this object was level with elevated content, and object (III) – soil with an addition of 30 $\text{mg} \cdot \text{kg}^{-1}$ soil d.m. of PAHs (10 mg BaP + 10 mg Ch + 10 mg Fl) + mineral salts, PAH quantity introduced to the soil on this object was equivalent to very strong pollution [13].

The experiment was conducted on the soil material of sandy silt loam grain size composition containing 26 % of the < 0.02 mm fraction. The soil material revealed a slightly acid soil reaction (pH H_2O = 6.27), hydrolytic acidity (Hh) assessed after soil extraction with 1 mol · dm^{-3} CH_3COONa solution was 23.9 mmol (+) · kg^{-1} of soil d.m. Organic carbon concentration was 15.99 g C · kg^{-1} of soil d.m. and total nitrogen 1.54 g N · kg^{-1} of soil d.m.

The pot experiment was conducted in PCV containers to which 8.6 kg of air-dried soil material was weighted. In order to meet the plant nutritional requirements, the soil of all objects, except the control (0), received nutrients in the form of chemically pure salts containing nitrogen, phosphorus and potassium. The quantities of nutrients (N, P, K) introduced per 1 kg of soil were respectively 0.12 g N (NH_4NO_3); 0.06 g P ($Ca(H_2PO_4)_2 \cdot H_2O$); 0.19 g K (KCl). The research was conducted in four replications; the soil material moisture during the vegetation period was maintained on the level of 60 % soil water capacity. The test plant was maize "San" c.v. Five plants per pot were kept until harvest which was done at the stage of 7–9 leaves.

Following maize shoots harvest, roots were taken from the soil lump, washed and then the plant material was dried in an air flow dryer (at 70 ^oC) until a constant weight in order to determine the dry weight. Subsequently, dried biomass was crushed in a laboratory mill and mineralized in a chamber furnace (at 450 ^oC for 5 hours). The residue was dissolved in a diluted nitric acid 1:2 (v/v) [14]. The content of studied trace elements was assessed in solutions prepared in this way by means of ICP-AES method on JY 238 Ultrace apparatus.

The quantities of absorbed trace elements was computed on the basis of biomass amounts and a component concentration in the biomass. On the basis of a total maize biomass (shoots and roots) the tolerance index was computed as a ratio of the plant yield dry mass in the objects 0, I, II and III and in the object where mineral medium was introduced to the unpolluted soil (object 0). The indicator of pollution degree was calculated on the basis of the element concentrations in plant shoots and as a ratio of the element content in plants from objects K, I, II and III and in the object in which a mineral medium was introduced to the unpolluted soil (object 0). Translocation coefficient was calculated as a product of the element content in plant shoots and roots [15].

Analysis of plant material was conducted in four replications. The precision of the assessments was determined using reference material NCS DC733448 (China National Analysis Center for Iron & Steel). The data concerning the precision and exactness of the assessments were given in Table 1 [16].

Table 1

Amounts (mean ±SD) of metals released for material NCS DC733448, as well as data for analytical precision and accuracy

Metal	The value obtained in current study [mg · kg^{-1} d.m.]	Recommended value [mg · kg^{-1} d.m.]	Precision	Accuracy
Pb	6.8 ± 0.1	7.1 ± 1.1	1.47	–4.22
Cd	0.18 ± 0.01	0.14 ± 0.06	5.55	28.57

The obtained results were elaborated statistically according to a constant model in which a factor was the level of PAH pollution. Conducted statistical computations considered a one-way ANOVA and the significance of differences between arithmetic means was estimated by means of t-Tukey's test at the significance level $\alpha < 0.05$ [17].

Results and discussion

The effect of soil pollution with PAHs on plant growth and development depends not only on the species but also, as stated by Maliszewska-Kordybach and Smreczak [18], mainly on the soil properties, primarily on its organic matter concentration. In the presented experiment, the amount of maize biomass in the objects where the soil was polluted with PAHs was bigger than on the control (unpolluted soil and without mineral salt supplement – object K) (Table 2). Therefore it may be stated that soil pollution with the analyzed PAHs did not inhibit maize growth or development. An analysis of maize biomass (shoots and roots) revealed the greatest amount in the object where the soil was characterized by a lower level of pollution – object II. Also Maliszewska-Kordybach and Smreczak [18] described a stimulating effect of PAHs on plant yield at the level of these substances below or slightly exceeding 1 mg · $kg^{-1}$of soil d.m. Kummerova et al [19] demonstrated that PAHs concentration not exceeding 10 mg · kg^{-1} d.m. in a solution may intensify plant biomass increment.

Table 2

The amount of biomass of maize [g d.m. · pot^{-1} ± SD] and the value of tolerance coefficient (mean ± SD)

Objects	Parts aboveground	Roots	Total biomass yield	Tolerance coefficient
K	$72.2^{a} \pm 4.0$	$12.6^{a} \pm 2.4$	$84.8^{a} \pm 6.3$	$0.58^{a} \pm 0.04$
0	$127.9^{b} \pm 4.1$	$17.6^{ab} \pm 1.1$	$145.5^{b} \pm 4.3$	1.00*
I	$135.3^{b} \pm 5.5$	$19.1^{ab} \pm 3.7$	$154.4^{b} \pm 9.1$	$1.06^{b} \pm 0.07$
II	$140.0^{b} \pm 7.0$	$20.4^{b} \pm 3.5$	$160.4^{b} \pm 10.0$	$1.10^{b} \pm 0.07$
III	$133.3^{b} \pm 1.9$	$17.8^{ab} \pm 0.9$	$151.2^{b} \pm 2.5$	$1.04^{b} \pm 0.03$

* Object 0 = 1.00. Means followed by the same letters in columns did not differ significantly at $\alpha < 0.05$ according to the t-Tukey test.

Beside the assessment of plant biomass quantity in conditions of increased stressor content in soil, also various other indices are being tested, which could more reliably show the effect of stress agent. The value of tolerance index in the objects where the stress agent was introduced (objects II and III) in the presented experiment was above one, which points to the absence of the effect of soil pollution with PAHs on the amount of plant biomass (Table 2). Lower than one value of the discussed index was noted only for the biomass from the control (the soil with natural PAH content and without the mineral medium – object K), which may be associated with a deficiency of available nitrogen, phosphorus and potassium forms. Aromatic hydrocarbons with bigger weights and molecular structures similar to gibberilines may affect plants as growth stimulators. The mechanism of plant growth stimulation at small concentrations of toxic substances is explained by a specific evolution of physiological control in organisms in result of which an excessive response to small deviations from standard are observed [20]. This phenomenon is also interpreted by increasing microbiological activity in result of which a biodegradation of polycyclic aromatic hydrocarbons occurs, which leads to an improvement in conditions for plant development [20, 21]. PAHs effect on plants may result from the soil properties. The result of elevated PAHs toxicity is observed in plants cultivated in soils poor in organic matter and in acid soils. On the other hand, lesser plant sensitivity is observed in soils abundant in organic matter or fertilized with it, which may result from a stronger PAHs sorption by this soil element [22–24], and therefore a lesser availability to plants [21–25].

Lead content in maize shoots did not exceed 0.50 mg · kg^{-1} d.m. Biomass from the objects where the soil was polluted with the analyzed hydrocarbons contained smaller amounts of this element (Table 3). Lead contents in the roots proved between over three and eight times higher, whereas the highest were registered in maize root system on the control (K). Like in the shoots, the least quantities of lead were assessed in maize roots from the object in which the soil was the most contaminated with PAHs (object III).

Table 3

Content of trace elements in maize biomass [mg · kg^{-1} d.m. ± SD]

Objects	Parts aboveground	Roots	Parts aboveground	Roots
	Cd		Pb	
K	$0.20^{a} \pm 0.01$	$2.57^{b} \pm 0.43$	$0.40^{b} \pm 0.06$	$3.11^{c} \pm 0.66$
0	$0.27^{a} \pm 0.05$	$1.43^{a} \pm 0.06$	$0.40^{b} \pm 0.10$	$2.50b^{c} \pm 0.44$
I	$0.43^{bc} \pm 0.02$	$1.02^{a} \pm 0.10$	$0.43^{b} \pm 0.10$	$1.59^{ab} \pm 0.34$
II	$0.37^{b} \pm 0.02$	$1.09^{a} \pm 0.07$	$0.26^{ab} \pm 0.04$	$2.07^{abc} \pm 0.42$
III	$0.47^{c} \pm 0.06$	$0.92^{a} \pm 0.13$	$0.19^{a} \pm 0.05$	$1.27^{a} \pm 0.27$

Means followed by the same letters in columns did not differ significantly at $\alpha < 0.05$ according to the t-Tukey test.

The amounts of lead taken up by maize shoots were the resultant of the biomass quantity and this element content (Table 4). Maize shoots absorbed the smallest quantities of lead in the object where the soil was contaminated by a bigger amount of the studied hydrocarbons (object III). A similar tendency was observed for maize root system.

Table 4

Uptake of trace elements with maize biomass [mg · pot^{-1} ± SD]

Objects	Parts aboveground	Roots	Parts aboveground	Roots
	Cd		Pb	
K	$0.014^{a} \pm 0.01$	$0.032^{b} \pm 0.01$	$0.029^{ab} \pm 0.01$	$0.041^{b} \pm 0.02$
0	$0.034^{b} \pm 0.01$	$0.025^{ab} \pm 0.01$	$0.051^{bc} \pm 0.01$	$0.044^{b} \pm 0.01$
I	$0.059^{c} \pm 0.01$	$0.019^{a} \pm 0.01$	$0.059^{c} \pm 0.01$	$0.032^{b} \pm 0.01$
II	$0.052^{c} \pm 0.01$	$0.022^{a} \pm 0.01$	$0.036^{abc} \pm 0.01$	$0.043^{b} \pm 0.02$
III	$0.063^{c} \pm 0.01$	$0.016^{a} \pm 0.01$	$0.026^{a} \pm 0.01$	$0.022^{a} \pm 0.01$

Means followed by the same letters in columns did not differ significantly at $\alpha < 0.05$ according to the t-Tukey test.

The index of maize shoot biomass pollution with lead was higher than one only in the object where dichloromethane (object I) was introduced to the soil, indicating lead accumulation in the biomass due to the applied agent (Table 5). The value of the discussed parameter for maize shoots from the other objects was much below one.

Table 5

The value of contamination coefficient parts aboveground of maize with trace elements (mean ± SD)

Objects	Cd	Pb
K	$0.43^{a} \pm 0.07$	$0.58^{a} \pm 0.08$
I	$1.79^{bc} \pm 0.48$	$1.27^{a} \pm 0.62$
II	$1.58^{bc} \pm 0.32$	$0.73^{a} \pm 0.16$
III	$1.91^{c} \pm 0.40$	$0.55^{a} \pm 0.22$

* Object 0 = 1.00. Means followed by the same letters in columns did not differ significantly at $\alpha < 0.05$ according to the t-Tukey test.

Lead translocation coefficient was much below one and did not reveal any significant diversification among the objects (Table 6), which evidences a lack of soil contamination with PAHs effect on this element migrations to maize shoots.

Table 6

The value of translocation coefficient trace elements (mean ± SD)

Objects	Cd	Pb
K	$0.08^{a} \pm 0.02$	$0.13^{a} \pm 0.03$
0	$0.19^{ab} \pm 0.04$	$0.16^{a} \pm 0.03$
I	$0.43^{cd} \pm 0.05$	$0.28^{b} \pm 0.06$
II	$0.34^{bc} \pm 0.03$	$0.13^{a} \pm 0.02$
III	$0.54^{d} \pm 0.14$	$0.16^{a} \pm 0.05$

Means followed by the same letters in columns did not differ significantly at $\alpha < 0.05$ according to the t-Tukey test.

Cadmium content in maize dry mass depended on the plant part and soil pollution with aromatic hydrocarbons (Table 3). More of this element was assessed in the root system. Maize shoots in the objects where dichloromethane was supplied to the soil and in the object where the soil was contaminated with benzo(a)pyrene, chrysene and fluorene contained significantly biggest cadmium quantities. Assuming that the value of $0.15 \text{ mg} \cdot \text{kg}^{-1}$ dry mass has been regarded as permissible in the biomass destined for consumption, the amount should be seen as considerably exceeded [26]. From the point of view of the biomass intended for fodder, cadmium concentration in the analyzed biomass did not raise objections. Maize root system contained much more of cadmium. The highest amounts were registered in root biomass from the control (K).

Amounts of cadmium taken up by maize shoots were significantly bigger in the objects in which aromatic hydrocarbons were supplied to the soil (II and III) and in the object in which dichloromethane was added to the soil (I). The amounts of cadmium taken up by maize root system were smaller, whereas maize root system absorbed the greatest quantities of cadmium in the control (K) (Table 4).

The indices of the degree of maize shoots pollution with cadmium were above one in all objects, except the control, whereas the highest value of this parameter was registered in the object where the soil was polluted with a bigger quantity of aromatic hydrocarbons (object III) (Table 5).

The values of translocation coefficient for this element were characterized by a relatively low diversification among the objects and confirmed a lower cadmium accumulation in maize shoots as compared with roots (Table 6).

Discussion of the research results of heavy metal content in maize in conditions of soil pollution with polycyclic aromatic hydrocarbons is made difficult by a limited number of literature positions addressing the presented issue. The problem of heavy metal bioavailability has been widely discussed in the aspect of these elements effect on biochemical processes occurring in a plant in the context of remediation of the chemically polluted lands, but also at the environmental application of waste materials [27–29]. Plants growing in the polluted environment may accumulate considerable amounts of toxic trace elements, which poses a serious hazard for animals and people [30, 31].

Heavy metal detoxification mechanisms developed by plants, after taking them up from soil solution allow these organisms to function in the polluted environment without any visible symptoms of phytotoxicity [7]. Many investigations demonstrated considerable differences in trace element uptake depending on the soil grain size composition, pH, organic matter content, or sorption capacity, however plant species is not without importance, either [26, 32]. According to Joung and Thorton [33] and Rosselli et al [34] increasing the soil pH value and organic matter content results in diminishing trace elements availability. However, Khan et al [35] and Young et al [36] call attention to the fact that trace element concentrations in plants may be also significantly influenced by the soil pollution with among others polycyclic aromatic hydrocarbons. The presented investigations make possible a statement that trace elements were accumulated mainly in maize root system. Investigations conducted by MacNicol and Beckett [37] confirm that roots constitute the first barrier restricting trace element translocation to the shoots, irrespectively of the stressor, although as stated by Batty and Anslow [38], there are plants which accumulate more of trace elements in the shoots. The barriers on the way of trace element transport from the roots to the shoots, generally act effectively in all plants towards lead. On the other hand, considering cadmium, they obviously depend on the cultivated plant species. According to Chu and Wong [39] such barriers exist also on the way of metal transport within the shoots. Batty and Anslow [38] revealed that soil contamination with pyrene did not reduce zinc uptake, nevertheless zinc and pyrene application to the soil markedly decreased Brassica juncea growth.

In the conducted experiment, cadmium concentrations in maize shoots were higher in the objects where dichloromethane and polycyclic aromatic hydrocarbons were introduced to the soil. As stated by Hart et al [40] higher content of cadmium in plant shoots may be connected with the role of phloem in this element transport to the shoots.

Conclusion

Soil pollution with the analyzed aromatic hydrocarbons did not inhibit either growth or development of maize roots or shoots. The greatest amount of biomass was obtained in the object where the soil was characterized by elevated content of the analyzed aromatic hydrocarbons . The value of tolerance index in the objects where stressor was introduced was above one, which indicates a lack of soil pollution with PAHs effect on plant biomass quantity. The value of tolerance index below one referred only to biomass from the control. Significant increase in Cd content and its quantities taken up by maize shoots was registered on the treatments where dichloromethane and polycyclic aromatic hydrocarbons were added to the soil in comparison with the unpolluted objects. The content and amounts of absorbed lead were the lowest on the object where the soil was the most polluted. Values of maize shoot biomass Cd pollution index were apparently higher in the objects where the soil was contaminated with polycyclic aromatic hydrocarbons in comparison with the values obtained in the object where soil received only mineral nutrient solution. Values of translocation index do not point to cadmium accumulation in plant shoots. Both the values of pollution index and translocation index for lead in the objects with elevated PAHs content in soil and in the object where the soil was contaminated with these substances were below one, which did not confirm excessive lead accumulation in maize shoots.

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WPŁYW ZANIECZYSZCZENIA GLEBY WWA NA ILOŚĆ BIOMASY KUKURYDZY ORAZ AKUMULACJĘ KADMU I OŁOWIU

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Abstrakt: Biodostępność pierwiastków śladowych ma kluczowe znaczenie w kwestii stymulacji lub hamowania procesów wzrostu i rozwoju roślin w późniejszych etapach ich życia, a w konsekwencji prowadzi do zmian wartości biologicznej biomasy np. ograniczając jej wykorzystanie. Ocenę wpływu sztucznego zanieczyszczenia gleby benzo(a)pirenem, chryzenem oraz fluorenem na ilość biomasy kukurydzy oraz akumulację w niej wybranych pierwiastków śladowych przeprowadzono w doświadczeniu wazonowym.

Zanieczyszczenie gleby badanymi węglowodorami aromatycznymi nie hamowało wzrostu i rozwoju części nadziemnych i korzeni kukurydzy. Największą ilość biomasy uzyskano w obiekcie, w którym gleba charakteryzowała się podwyższoną zawartością badanych węglowodorów aromatycznych. Wartość wskaźnika tolerancji w obiektach, w których wprowadzono czynnik stresowy, kształtowała się powyżej jedności, co wskazuje na brak wpływu zanieczyszczenia gleby benzo(a)pirenem, chryzenem oraz fluorenem na ilość biomasy roślin. Wartość wskaźnika tolerancji poniżej jedności dotyczyła jedynie biomasy z obiektu kontrolnego. Istotnie większe zawartości Cd oraz ilości pobrane tego pierwiastka przez części nadziemne kukurydzy stwierdzono w obiektach, w których do gleby wprowadzono dichlorometan i wielopierścieniowe węglowodory aromatyczne w porównaniu do obiektów niezanieczyszczonych. Zawartość i ilości pobranego ołowiu były najmniejsze w obiekcie, w którym gleba była najbardziej zanieczyszczona. Wartości wskaźnika zanieczyszczenia biomasy części nadziemnych kukurydzy Cd były wyraźnie większe w obiektach, w których glebę zanieczyszczono węglowodorami aromatycznymi w porównaniu do wartości, jakie uzyskano w obiekcie, w którym do gleby wprowadzono tylko pożywkę mineralną. Wartości wskaźnika translokacji nie wskazują na nagromadzenie kadmu w częściach nadziemnych roślin. Zarówno wartości wskaźnika zanieczyszczenia, jak również wskaźnika translokacji dla ołowiu, w obiektach o podwyższonej zawartości WWA w glebie oraz w obiekcie, w którym glebę skażono tymi substancjami kształtowały się poniżej jedności nie potwierdzając nadmiernego nagromadzenia ołowiu w częściach nadziemnych kukurydzy.

Słowa kluczowe: gleba, zanieczyszczenie, wielopierścieniowe węglowodory aromatyczne, kadm, ołów

DOI: 10.2428/ecea.2013.20(04)051 ECOL CHEM ENG A. 2013;20(4-5):545-554

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EFFECT OF BIOREMEDIATION OF OIL DERIVATIVES IN SOIL ON *Pterostichus* sp. (COLEOPTERA, CARABIDAE) OCCURRENCE

WPŁYW BIOREMEDIACJI ROPOPOCHODNYCH W GLEBIE NA WYSTĘPOWANIE *Pterostichus* sp. (COLEOPTERA, CARABIDAE)

Abstract: The research aimed at investigating the effect of oil derivatives during the process of their bioremediation on dynamics of *Pterostichus* sp. (Coleoptera, Carabidae) occurrence. The following objects were established in two series (natural and supported bioremediation): control – unpolluted soil; soil polluted with petrol; soil polluted with diesel fuel and soil polluted with used engine oil (dose: 6000 mg of fuel · kg^{-1}d.m. of soil). Epigeal fauna was trapped using Barber's traps. During the periods from June to October 2010, from May to October 2011 and in May and June 2012 the traps were emptied once a week.

Soil pollution with petrol inhibits *Pterostichus* sp. beetles activity for about 3 months, whereas diesel oil may reveal a negative effect even after 14 months, and engine oil after 13 months from the moment of pollution. Bioremediation process of soil contaminated with oil derivatives generally does not affect *Pterostichus* beetles during the first 5 months after its initiation, but after a year it may contribute to increased activity under conditions of soil polluted with diesel oil. The COD data indicate that the process of bioremediation occurs in all of the tested soil samples. It was the most intensively in the case of soil polluted with used engine oil.

Keywords: oil derivatives, soil, bioremediation, Carabidae, *Pterostichus* sp.

Oil derivatives belong to widespread soil pollutants. Their source may be leaks from storage containers, pipeline damage, road accidents, mechanization of agriculture,

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industries, etc. [1]. Moreover, for many years petroleum sprays were used as insecticides [2].

The effect of oil derivatives on invertebrates depends on pollutant concentration, their kind, the time during which animals are exposed to them and on animal species [3, 4]. Investigations conducted so far revealed that oil derivatives in soil negatively affect the representatives of epigeal fauna, including carabid beetles. Their considerably limited presence was observed in polluted areas [5–8] whereas the time of negative influence depended on the pollutant.

Carabid beetles of *Pterostichus* sp. genus are counted among the most common species, both on arable fields and in forests. They are typical predators, although their occasional uptake of plant feed was also reported [9]. Research on pollutant influence of these invertebrates focuses mainly on heavy metal effect. They reveal that detoxification methods used by *Pterostichus* sp. beetles allow to limit heavy metal accumulation [10, 11], however some metals, *eg* copper depressed locomotor activity, which may reduce the fitness of the animal under field conditions. Investigations on the effect of petrol, diesel fuel and engine oil on life and biochemical parameters of *Pterostichus cupreus* L. species demonstrated declined survivability at the exposure to diesel fuel and changes in activity of some detoxifying enzymes under the influence of diesel and engine oil [12]. Microbial biopreparations used to support natural process of oil derivative pollutants degrading may affect the subsequent links of trophic chain through changes of bacterial flora and formation of short chained intermediates in result of their activity. Changes in number of some arachnid groups were registered after their application [13, 14].

The work aimed at investigating the effect of oil derivatives during the process of their bioremediation on dynamics of *Pterostichus* sp. (Coleoptera, Carabidae) occurrence.

Material and methods

The investigations were conducted in 2009–2012 at the Experimental Station of the University of Agriculture in Mydlniki near Krakow. In autumn 2009 indigenous soil was placed in 1 m^3 containers with maintained natural layers arrangement.

The containers were then dug into the soil, so that their upper area was on the same level with the surrounding soil. The soil in containers was left untouched for 8 months to allow it to restore its natural biological efficiency. Subsequently, in June 2010 the soil in containers was polluted with the following oil derivatives: petrol, diesel oil and used engine oil in the amounts equal to 6000 mg of fuel $\cdot$ kg^{-1} d.m. of soil. A week later half of the containers was subjected to bioremediation with the use of ZB-01 biopreparation, specially prepared for this purpose. Four objects were identified in each of the two series (natural and supported bioremediation): 1. Control – unpolluted soil, 2. Soil with simulated petrol leak, 3. Soil with simulated diesel oil leak and 4. Soil with simulated used engine oil leak. The whole experiment was conducted in 4 replications according to randomized block design. Epigeal fauna was trapped using Barber's traps (0.9 dm^3 jars dug even with the soil level and protected against atmospheric precipitation with a plastic roof) placed in the central point of each container. During the periods from June to October 2010, from May to October 2011 and in May and June 2012 the traps were emptied once a week. Trapped carabid beetles were classified using appropriate keys [15].

In order to monitor total pollutant load, measurements of *chemical oxygen demand* (COD) were made in samples according to Polish Standard [Polska Norma PN-74 C-04578/03]. For this reason the soil was dried until constant weight at room temperature. Air-dried soil was averaged and rubbed through a sieve with 0.1 mm mesh. Subsequently an appropriately selected soil weighed portion was suspended in distilled water. The assessments were made using cuvette tests LCK-ChZT (with measuring range 1000–60000 mg/dm^3) made by Hach-Lange. The required sample amount (from 0.2–0.5 cm^{3}of sample depending on measuring range of applied cuvette tests) with suspended soil was removed to measuring vial, which was then placed in Hach-Lange mineralizer for mineralization (at 148 ^{o}C for 2 hours). In order to inhibit oxidation reaction, the cuvettes were cooled under cold running water. Subsequently, COD measurement was conducted by means of DR 5000 Spectrophotometer (Hach-Lange). The final results were given in mg of oxygen per 1 kg of air-dried soil.

Statistical computations concerning *Pterostichus* sp. beetles occurrence in the subsequent months from the moment of soil pollution were made using Statistica 9.0 PL computer programme. Means were diversified using LSD Fisher test at significance level $\alpha = 0.05$.

Results and discussion

Pterostichus sp. beetles revealed the highest activity in August (Fig. 1 and 2). At that time, on average even 6 specimens per week were trapped into one trap.

In the 2010 season, *ie* after 0 to 5 months from the moment of soil pollution, beetles were more numerously trapped under conditions of control soil (Fig. 1). At the same time a negative effect of applied supported bioremediation on their activity under conditions of unpolluted soil was visible. The applied ZB-01 biopreparation includes the nutrients and substrate for microorganisms. The relatively low concentration of petroleum as a substrate can influence the activities of *Pterostichus* sp. in terms of their settle in unpolluted control soil. As can be seen in Table 1, the above-mentioned effect is noticeable up to four months of the experiment's duration. After that time the influence of the substrate disappears and the soil regains the properties as a control one (0R). Soil contamination with petrol and diesel fuel contributed to limiting *Pterostichus* sp. beetles activity for 3 months, whereas in case of engine oil a marked decline in the number of trapped beetles was noted in the second and third month. In the last above-mentioned object applied ZB preparation reduced the activity of investigated animals in the second month after its application, whereas in the other objects with contaminated soil no significant effect of supported bioremediation was observed. Beetles' activity in the 4th and 5th month (*ie* September and October) was slight and therefore no marked influence of the applied oil derivatives or applied bioremediation

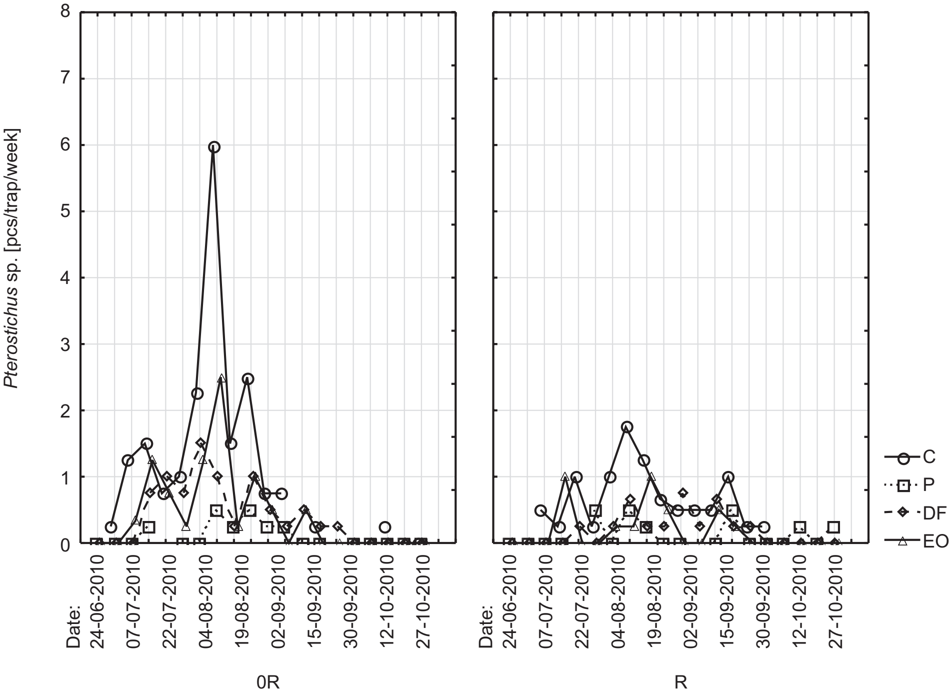

Fig. 1. Course of dynamics of *Pterostichus* sp. occurrence trapped using Barber's traps in 2010. EO – soil contaminated with used engine oil, DF – soil contaminated with diesel fuel, P – soil contaminated with petrol, C – unpolluted soil, 0R – series with natural bioremediation, R – series with supported bioremediation

was observed. In previous research using oil derivatives dose of 2 dm^3/m^2 *Pt. vulgaris* species reduced its activity in the area polluted with petrol and diesel fuel for one month, whereas in the area polluted with engine oil in one of two years of investigations, the first beetles were trapped only after 3 months [8]. Laboratory analyses of the oil derivative effect on life and biochemical parameters of *Pt. cupreus* beetles using the soil from the presented experiment, collected in August 2010 (3rd month from the moment of soil pollution) revealed that diesel oil contributed to lowering their survivability by 31 % in comparison with the control, soil contamination with engine oil proved less toxic (6 % of the insects died), whereas petrol had no effect on this beetle survival. The investigated substances did not have any influence on beetle body weight, but they caused a decline in the activity of microsomal enzyme ECOD (*Ethoxycoumarin-O-deethylase*). Moreover, in comparison with control data, a decrease in superoxide dismutase and HSP70 proteins level in beetles exposed to used engine oil and increase in glutathione transferase activity in beetles exposed to diesel oil were noticed [12].

In the 2011 season, *ie* after 11–16 months from the moment of soil pollution, the dynamics of *Pterostichus* sp. beetles occurrence pointed to consistent negative influence of soil pollution with diesel and engine oil, whereas the number of beetles trapped under

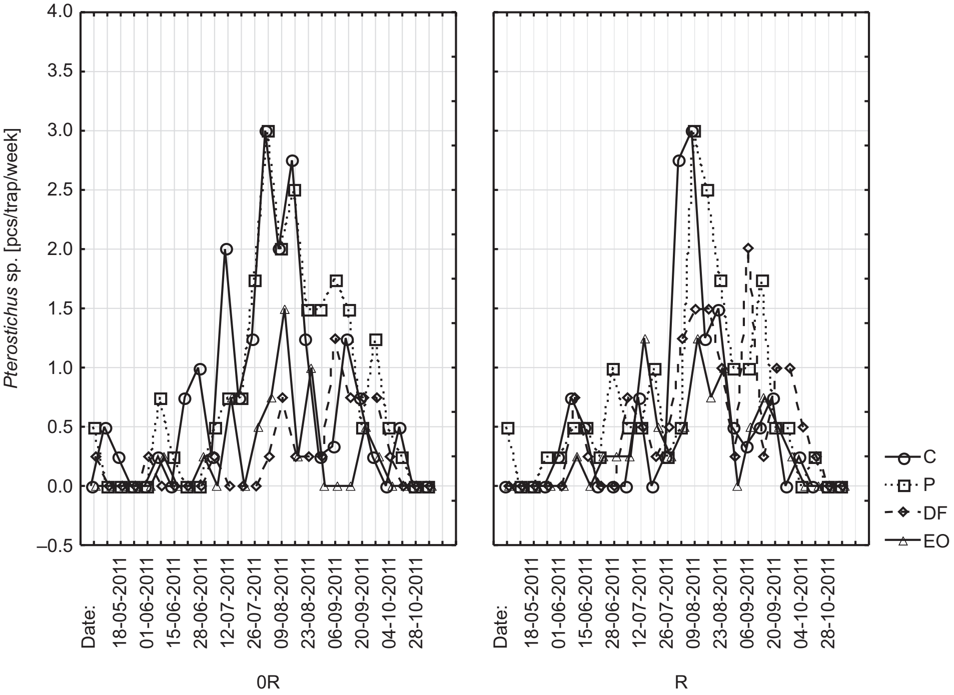

Fig. 2. Course of dynamics of *Pterostichus* sp. occurrence trapped using Barber's traps in 2011. The symbols as in Fig. 1

conditions of petrol polluted soil was similar as in the control (Fig. 2). A significant decrease in the number of trapped beetles was registered under conditions of soil contaminated with diesel oil in the months from 12 to 14 and in engine oil polluted soil in the 13th month (*ie* during the period of their highest activity) (Table 1). Starting from the 12th month a beneficial effect of supported bioremediation applied on the soil polluted with diesel oil towards the number of trapped beetles was visible. At the same time slightly more of the investigated animals were trapped also under conditions of soil contaminated with engine oil and inoculated with ZB-01 preparation as compared with the same object where the treatment was not applied.

In the 2012 season insects were trapped in May and June (23rd and 24th month since the moment of the soil contamination). Carabid activity at that time was slight (Fig. 3). In most cases no significant differences were observed between studied objects depending on the kind of pollution, or applied supported bioremediation. Only in the object where the soil was polluted with diesel fuel, more trapped beetles were noted than under conditions of unpolluted soil.

Previous investigations revealed that in the area contaminated with crude oil in result of a road accident and subjected to bioremediation, even after 3 years from the moment of pollution occasionally lower number of trapped *Pterostichus* sp. beetles was noted than on the control [16].

Table 1

Occurrence of *Pterostichus* sp. trapped using Barber's traps in individual months after soil contamination. The symbols as in Fig. 1

Number of months from the moment of soil contamination	*Pterostichus* sp. [pcs/trap/month]							
	Control		Petrol		Diesel fuel		Engine Oil	
	0R	R	0R	R	0R	R	0R	R
1	3.00 c*	0.75 ab	0.25 ab	0.00 a	0.75 ab	0.00 a	1.58 bc	1.00 ab
2	9.08 d	4.00 bc	0.50 a	1.00 ab	4.25 bc	1.08 ab	4.75 c	0.50 a
3	5.50 c	2.92 b	1.25 ab	0.25 a	2.00 ab	1.50 ab	1.75 ab	1.50 ab
4	0.25 a	2.00 b	0.00 a	0.50 ab	1.00 ab	1.17 ab	0.50 ab	0.75 ab
5	0.25 a	0.00 a	0.00 a	0.50 a	0.00 a	0.00 a	0.00 a	0.00 a
11	0.75 a	0.25 a	0.50 a	1.00 a	0.50 a	0.00 a	0.00 a	0.00 a
12	2.00 b	1.25 ab	1.00 ab	2.25 b	0.00 a	1.00 ab	0.50 ab	0.75 ab
13	4.25 c	1.00 a	3.75 bc	2.25 abc	0.25 a	2.00 ab	1.25 a	2.25 abc
14	9.25 bc	9.00 bc	10.50 c	8.75 bc	1.75 a	5.50 abc	3.50 ab	3.50 ab
15	2.58 abc	1.58 ab	5.00 c	3.75 abc	3.50 abc	4.25 bc	0.75 a	2.00 abc
16	0.50 a	0.25 a	0.75 a	0.25 a	0.25 a	0.75 a	0.00 a	0.00 a
23	0.50 a	0.50 a	1.25 ab	1.00 ab	1.92 b	1.50 ab	0.25 a	0.75 ab
24	0.75 a	3.25 a	2.50 a	2.25 a	2.25 a	1.50 a	1.50 a	2.75 a

* Means in lines marked with the same letters do not differ significantly according to LSD test at $\alpha = 0.05$; factors contamination × remediation.

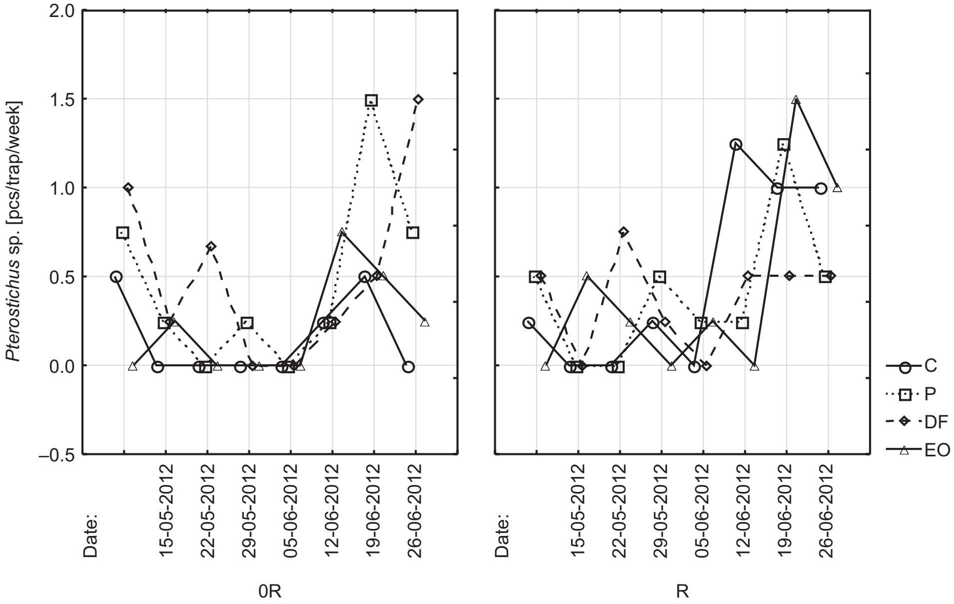

Fig. 3. Course of dynamics of *Pterostichus* sp. occurrence trapped using Barber's traps in 2011. The symbols as in Fig. 1

Figure 4 shows changes of COD parameter in the soil contaminated with used engine oil, diesel oil and petrol in comparison with the control sample (unpolluted soil). In case

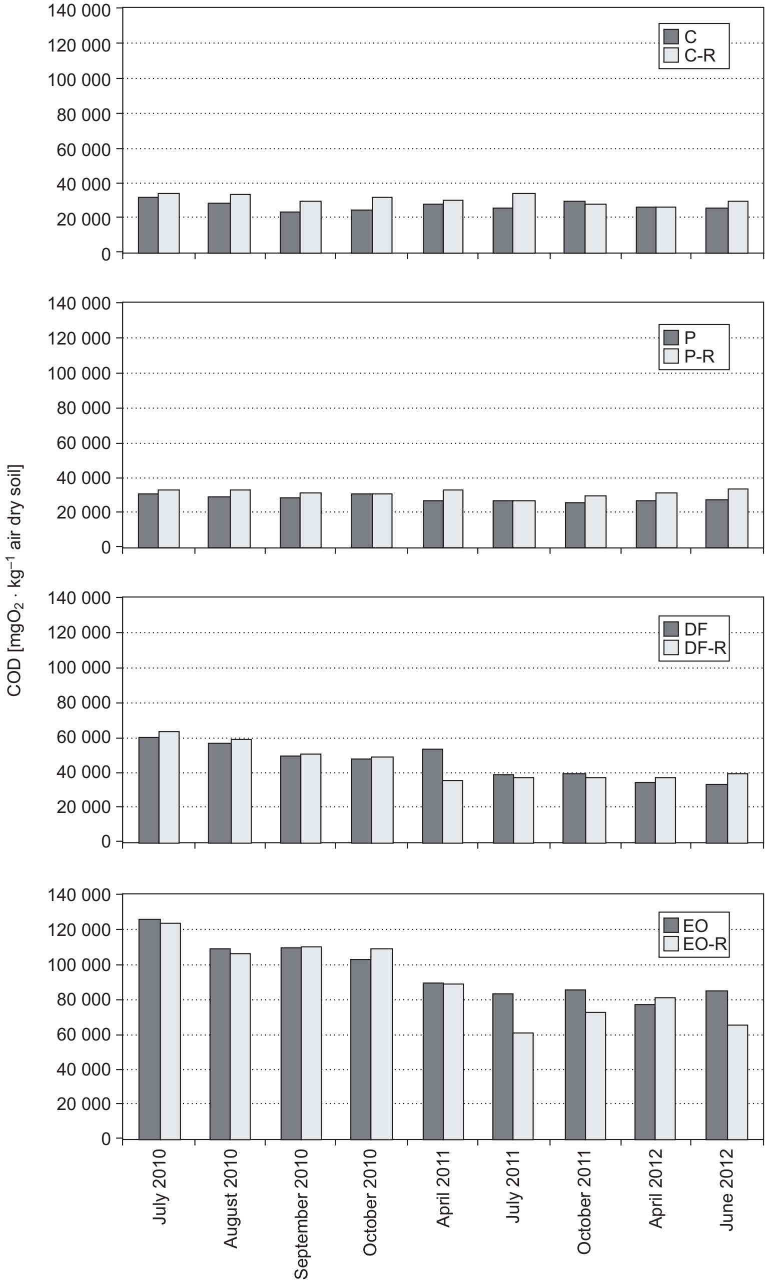

Fig. 4. Dynamics of COD changes during biodegradation process. The symbols as in Fig. 1

of samples of soil contaminated with used engine oil, both subjected to bioremediation supported with ZB-01 preparation and natural bioremediation, the highest initial value of COD parameter was registered on the level of *ca* 126 000 $mgO_2 \cdot kg^{-1}$ of air-dried soil. In course of microbial bio-cleaning process, a dynamic decline of this parameter value to the level of *ca* 85 000 and 65 000 $mgO_2 \cdot kg^{-1}$ of air –dried soil was registered respectively for the soil subjected to natural bioremediation and supported bioremediation. In the variant with diesel oil, like in the soil contaminated with used engine oil, a dynamic decrease in COD parameter value was noticed (from *ca* 60 000 to 35 000 $mgO_2 \cdot kg^{-1}$ of air-dried soil).

Kinetics of COD value changes deserves attention, since it shows that in case of soil subjected to supported bioremediation process (introducing ZB-10 preparation inoculums), already in the 10th month COD value was significantly lower than COD value for soil sample from natural bioremediation process (without inoculation). It may indirectly point to more efficient biodegradation of oil derivatives in case of the sample treated with ZB-01 biopreparation.

Observation of changes of COD parameter for the soil contaminated with petrol points to its fluctuations on the level of *ca* 30 000 (for not inoculated soil) and 32 000 (for inoculated soil). These changes seem to be random and are not connected with process of oil derivatives degradation.

Conclusions

1. Soil pollution with petrol inhibits *Pterostichus* sp. beetles activity for about 3 months, whereas diesel oil may reveal a negative effect even after 14 months, and engine oil after 13 months from the moment of pollution.
2. Bioremediation process of soil contaminated with oil derivatives generally does not affect *Pterostichus* beetles during the first 5 months after its initiation, but after a year it may contribute to increased activity under conditions of soil polluted with diesel oil.
3. The COD data indicate that the process of bioremediation occurs in all of the tested soil samples. However, in the case of soil contaminated with petrolum and diesel oil the COD measurments provide the information about the orginal content of the organic matter and the one being artificially introduced into soil. The above conclusion has been drawn out on the basis of weight method (data not shown). Only when the soil is contaminated with engine oil, do COD data illustrate the bioremediation process with more oxygen being required for the oxidation rection of organic matter.

Acknowledgement

Scientific publication financed from the funds for science in 2009–2012 as a research project (N N305 151537).

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WPŁYW BIOREMEDIACJI ROPOPOCHODNYCH W GLEBIE NA WYSTĘPOWANIE *Pterostichus* sp. (COLEOPTERA, CARABIDAE)

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Abstrakt: Celem pracy było zbadanie oddziaływania substancji ropopochodnych w trakcie procesu bioremediacji gleby na dynamikę występowania chrząszczy z rodzaju *Pterostichus* sp. (Coleoptera, Carabidae).

W ramach doświadczenia utworzono następujące obiekty w dwóch seriach (z naturalną bioremediacją i stymulowaną bioremediacją): 1. Kontrola – gleba niezanieczyszczona. 2. Gleba z symulowanym wyciekiem benzyny, 3. Gleba z symulowanym wyciekiem oleju napędowego, 4. Gleba z symulowanym wyciekiem zużytego oleju silnikowego w dawce 6000 mg substancji ropopochodnej · kg^{-1} s.m. gleby. Odłowy fauny naziemnej prowadzono z wykorzystaniem pułapek Barbera. W okresach od czerwca do października 2010, od maja do października 2011 oraz w maju i czerwcu 2012 r. pułapki opróżniano raz w tygodniu.

Zanieczyszczenie gleby benzyną ogranicza aktywność chrząszczy z rodzaju *Pterostichus* przez okres ok. 3 miesięcy, natomiast olej napędowy może wykazywać negatywny wpływ jeszcze po upływie 14 miesięcy, a silnikowy po upływie 13 miesięcy od momentu zanieczyszczenia. Proces bioremediacji gleby zanieczyszczonej ropopochodnymi na ogół nie wpływa na aktywność biegaczowatych z rodzaju *Pterostichus* w ciągu pierwszych 5 miesięcy po jego zainicjowaniu, natomiast po upływie roku może przyczyniać się do wzrostu aktywności w warunkach gleby zanieczyszczonej olejem napędowym. Analiza parametru ChZT wskazuje, że proces bioremediacji przebiegał we wszystkich próbkach gleby, najintensywniej w przypadku gleby zanieczyszczonej olejem silnikowym.

Słowa kluczowe: ropopochodne, gleba, bioremediacja, Carabidae, *Pterostichus* sp.

DOI: 10.2428/ecea.2013.20(04)052 ECOL CHEM ENG A. 2013;20(4-5):555-563

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STUDY ON BIOAVAILABILITY OF LEAD FROM PRODUCTS OF PHOSPHATE ROCK ACIDULATION OBTAINED BY PAPR TECHNIQUE

BADANIE PRZYSWAJALNOŚCI OŁOWIU W PRODUKTACH ROZKŁADU SUROWCÓW FOSFOROWYCH TECHNIKĄ PAPR

Abstract: Use of phosphate fertilizers in the world constantly decreases in the last few years. The reason is increase of a unit prices of nutritious components what results in automatic growth of phosphate fertilizers prices. It is a well-known fact that phosphorus in a fertilizer causes not only growth but also a stabilization of plant production. That's why economic aspects exacted a necessity of searching cheaper resolutions for plant fertilization. Fertilizers containing partially acidulated phosphate rock like PAPR show long-lasting activity thanks to content of phosphorus with different solubility extent. Therefore, they can be an alternative for present sources of phosphorus like superphosphate. Very important is an optimization of PAPR composition. Content of macro- and microelements like zinc, manganese, copper, iron determine usefulness of definite preparation for fertilization goals. Knowledge of heavy metals concentration in given fertilizer may turn out fundamental if we are talking about ecological and healthy aspects of using partially acidulated phosphate rocks. Products type PAPR were made in laboratory by dissolving phosphate rocks with non-stoichiometric quantity of sulphuric acid. Next mineralization of appropriate fertilizer weighted amount was conducted in the aim of determine heavy metal concentration. Lead content in fertilizers type PAPR was studied in Autolab device using differential pulse voltammetry method.

Keywords: partially acidulated phosphate rock, heavy metals, lead, voltammetry

Introduction

Poland is an important producer of mineral fertilizers not only in Europe but also in the world. National industry brings about 1.5 % of world production of nitric fertilizers and about 1.6 % of phosphate fertilizers [1]. Poland is a second producer (after Russia) of phosphate fertilizers in an European scale [2]. The observed trend of increasing

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nutrient unit prices meant that at the turn of 2007/2008 was reached record prices of mineral fertilizers, which resulted in large instability of fertilizer sector in Poland and worldwide. In the second half of 2008, as a result of drastically deteriorating relations between fertilizers prices to grain prices and also expected weakening of demand for food due to financial crisis, there has been a clear breakdown in the fertilizers market. Then, for the first time in several years, wasn't observed the increasing tendency for the global use of mineral fertilizers, and the main reason was the sharply reduce their purchases in the second half of 2008 [3]. The food production is inseparably connected with using fertilizers in agriculture, so the aspect of economic production of phosphate fertilizers as well as modification of existing technologies for their manufacture should be taken into consideration.

Partially acidulated phosphate rocks

In recent years PAPR-type fertilizers (partially acidulated phosphate rocks) have become a prospective alternative to existing sources of phosphorus, such as superphosphates. phosphate, have recently become a PAPR fertilizers (partially acidulated phosphate rocks). They are formed by partial acidulation of phosphate rock through the use of nonstoichiometric amount of sulfuric or phosphoric acid (or their solution in the appropriate ratio – optionally).

Reactions of receiving the PAPR fertilizers can be divided into stages and described using chemical reactions [4].

Stage I: The reaction takes place on the surface of ground phosphate rock grains. Using in the initial stage of reaction the excess of sulfuric acid, we receive phosphoric acid in the first place:

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + aq = 5CaSO_4 - 0.5H_2O + 3H_3PO_4 + aq + HF \quad (1)$$

Stage II: In this stage phosphoric acid reacts with undecomposed to this point fluoroapatite:

$$Ca_5F(PO_4)_3 + 7H_3PO_4 + aq = 5Ca(H_2PO_4)_2 \cdot H_2O + aq + HF \quad (2)$$

Degree of PAPR stoichiometric norm is a parameter expressing the proportion of the quantity of mineral acid used in the process to the quantity of acid, which results from the stoichiometric reaction of PR dissolution. This factor can be expressed by the formula [5]:

$$\eta_{PAPR} = \frac{\eta^{r}_{PAPR}}{\eta^{s}_{PAPR}} \quad (3)$$

where: η_{PAPR} – degree of PAPR stoichiometric norm,
η^{r}_{PAPR} – actual quantity of mineral acid used in the process,
η^{s}_{PAPR} – quantity of acid results from the stoichiometric reaction.

Degree of PAPR stoichiometric norm is typically less than one, and for the stoichiometric reaction with complete PR dissolution takes a value equal one; this coefficient is dimensionless.

Partially acidulated phosphate rocks, sulphuric or phosphoric acid are mostly cheaper counting the total phosphorus than other phosphate fertilizers. It is caused by the less use of acids during obtaining the product, additionally PAPR fertilizers usually contain more phosphorus than single superphosphate. Another advantage of using partially acidulated phosphate rocks is the fact that they have a higher tolerance for lower quality rock phosphate, which can not be used for the production of superphosphate [4]. Using this type of fertilizers is economically more profitable and also phosphorus from the PAPR type fertilizer remains longer in soil as a dicalcium phosphate, which is better absorbed by plants [6].

Heavy metals

Soil contamination with heavy metals constitutes nowadays a serious problem of developed countries [7]. High concentration of heavy metals in soils may cause not only the risks to ecosystems, but also for the people. The total natural content of heavy metals in soil depends primarily on the type of parent rock and special soil factors. The content of individual elements in the soil is determined by the impact anthropogenic and climatic factors [8]. Cultivated soil and fertilizers are known to contain some amounts of heavy metals such as cadmium, copper, lead, mercury, derived mainly from anthropogenic sources. Average content of heavy metals in phosphate fertilizers can be presented in the following order: Cd < Cu < Pb < Ni < Zn. Although we should remember about a great variety of heavy metals level concentrations depending on the type of fertilizer, in addition various is the degree of solubility and availability of heavy metals in plants in phosphate fertilizers [8]. Due to negative impact of these compounds on human health, it is recommend to reduce their level in fertilizers using appropriate monitoring of the concentration in raw materials and also in manufactured fertilizers [7, 9].

Lead in soil and fertilizers

Lead, one of the well-explored heavy metals, constitutes a major threat to human health [10]. Average natural content of lead for Polish soils is 18 ppm, and it is assumed that the natural content of this metal for most soils should not exceed 20 ppm [11]. In a result of weak lead migration, its natural distribution in soil profile reflects its content in parent rocks. However, the availability of lead in the surface soil layers is mainly connected with the influence of anthropogenic factors and is generally overestimated in relation to its natural content. In general, lead isn't mobile in soils. This metal rarely occurs in the form of cation Pb^{2+}, but he creates the ions complex, such as $Pb(OH)^+$ and $Pb(OH)^{4+}$, which mostly regulate the sorption and desorption processes. In acid soils dominate the organic forms of lead, which can both decrease or increase its migration. Mobile forms of lead in acid soils occur mainly as Pb^{2+} and $PbHCO_3^+$ or organic complexes. In alkaline soils dominate: $Pb(OH)^+$ and $Pb(CO_3)_2^{2-}$. Leadis strongly immobilized by most soil components: loamy minerals, Fe and Al hydroxides, and organic substance. Lead precipitation to carbonates and phosphates is an important process , which decides of its immobilization in soils at pH > 6.5. The increase of lead content in the surface soil layers unfavorably influences the microflora and microfauna, because higher concentration of this metal inhibits the decomposition of organic matter, which ultimately causes the degradation of the soil. This metal is particularly decomposed in phosphate raw minerals, which can accumulate up to a content of approximately 30 % w/w of PbO. The content of this element in phosphate rocks used to produce phosphate fertilizers determines its concentration in the manufactured fertilizer materials. That is why important is not only the economic aspect of using different solutions in the production of phosphate fertilizers, but also the guarantee that the received fertilizer brings the smallest potential threat to ecosystems and human health. It should be remembered that even a small amount of lead put into the human body with food can cause the nervous system disorders, and chronic lead poisoning leads to brain damage, coma or even death [12]. Lead in soils and the control of its content in applied fertilizers is a subject of many researches, which basic goal is to define its bioavailability, the migration to ground waters, toxicity to organisms and the degree of incorporation into the food chain [11].

Materials and methods

The aim of the studies was to investigate the lead content in a PAPR-type fertilizer formulations using differential pulse voltammetry method in accordance with Polish Standard PN-92, C-87070/05. The method consisted in wet digestion of lead compounds found in the sample of the fertilizer solution using perchloric acid, and then receiving the metal peak by voltammetry method through analysis and interpretation of the graph [13, 14]. To product PAPR fertilizer we used samples of 50 g phosphate rock ZIN, which was dissolved with a stoichiometric amount of sulfuric acid to give products of varying degrees of PAPR stoichiometric norm $\eta_{PAPR} = 0.1, 0.2, 0.3, 0.4$ and 0.5.

Fertilizer formulations were produced in a laboratory reactor Syrris Atlas, which allow to control the temperature and process time, pH and mixing rate. After the reaction the fertilizer preparation was dried at room temperature for approximately 24 h before the mineralization.

In order to prepare phosphate fertilizers samples for voltammetric researches, approximately 3 g of the fertilizer was weighted, 10 cm^3 of perchloric acid was added, and the contents of the beaker was heated to boiling until a clear brightening solution was given. Then the 5 cm^3 of distilled water was added to the beaker, again heated to boiling, and after cooling, the contents of the beaker were transferred quantitatively to a volumetric flask and made up 100 cm^3 with distilled water. The prepared solution was mixed and filtered again, and from the filtrate samples were taken for further analysis. Determination of lead content were performed in flasks with a capacity of 50 cm^3, to which were entered: 25 cm^3 of a basic electrolyte (78 g sodium chloride and 53 g sodium hypophosphite dissolved in a volumetric flask of capacity 1 dm^3), 1 cm^3 of

0.1 % w/w gelatin solution in order to minimize electric noises, and 4, 6, 8 or 10 cm^3 of earlier prepared solution of fertilizer samples. Lead concentration in PAPR type fertilizers was studied in Autolab device using differential pulse voltammetry method. Lead peaks were recorded in the potentials from –0.2 to –0.7 V, gaining the most pronounced peaks of lead at the half-wave around –0.38 V.

Additionally, in manufactured PAPR fertilizers were made an extraction of water-soluble phosphorus and total phosphorus extraction with a mixture of hydrochloric and nitric acid according to Polish Norm PN-88, C-87015 [15, 16].

Water soluble phosphorus

Approximately 1g of fertilizer sample was added to the 500 cm^3 flask, then 400 cm^3 of water was poured and the flask was placed into the rotational set where it was shaken for 0.5 h at 45 rpm. Then a flask was filled up with distilled water and carefully mixed. After the residue precipitate the solution was filtered through the dry filter into dry vessel. Phosphorus concentration was measured in the water phase.

Total phosphorus

Fertilizer sample 1 g was added to 400 cm^3 beaker. Then 50 cm^3 of the nitric and hydrochloric acid mixture at 3:1 ratio (v/v) was poured into the beaker. The solution was heated to boiling for 0.5 h. After this time 100 cm^3 of water was added and boiled again for 15 minutes. When the mixture was cooled it was transferred quantitatively to the 500 cm^3 flask, carefully mixed and filtered to the dry vessel rejecting about 50 cm^3 of the first part of the filtrate.

Spectrophotometric analysis

Samples of 1 cm^3 from the received filtrate was added to the 100 cm^3 flask. Next the 20 cm^3 of the vanadate-molybdate complex and the distilled water were poured to the flask. Solutions were left for 15 minutes at room temperature. After this time absorbance was measured at 430 nm wave-length using spectrophotometer of the JASCO company. Phosphorus content in the analyzed fertilizers samples was found from the calibration curve which was prepared in earlier investigations.

Results and discussion

Table 1 describes the average concentration of lead for varying degree of PAPR stoichiometric norm, calculated in accordance with the formula in the Polish Norm PN-92/C-87070/05.

Additionally the content of lead in phosphate rock ZIN was measured, the preparing procedure was the same as for the PAPR type fertilizer samples [PN-92/C-87070/05]. For the phosphorous material concentration of lead was equal to: 1.00375 μg/g.

Table 1

Average lead content in PAPR-type fertilizer formulations of various degrees of PAPR stoichiometric norm

Sample No.	η_{PAPR}	Lead content [μg/g]
1	0.1	0.364
2	0.2	0.368
3	0.3	0.375
4	0.4	0.487
5	0.5	0.948

The investigations revealed that increased values of lead content in obtained fertilizer samples were followed by raising the η_{PAPR} value. The lead content in ZIN phosphate rock is higher in comparison with the PAPR-type formulations.

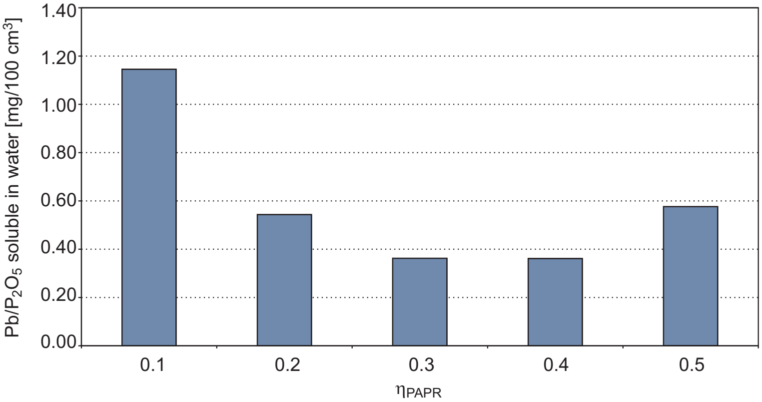

Fig. 1. Comparison of the content ratio of lead to phosphorus soluble in water [$\alpha = Pb/P_2O_5$ (μg/g)/(mg/100 cm^3)] in relation to various degree of PAPR stoichiometric norm

The lead content in obtained PAPR-type fertilizers were compared with a P_2O_5 content by calculating the α coefficient. Coefficient α was obtained by dividing the concentration of lead (Table 1) by the content of water soluble phosphorus or total phosphorus (Table 2) in a PAPR-type fertilizers:

$$\alpha = \frac{Pb}{P_2O_5} \left[\frac{\mu g / g}{mg / 100\ cm^3}\right] \tag{4}$$

where: Pb – concentration of lead in a sample of PAPR-type fertilizers [μg/g],
P_2O_5 – content of water-soluble or total phosphorus in PAPR – type fertilizers [mg/100 cm^3].

Table 2

Content of P_2O_5 soluble in water and a mixture of HNO_3 + HCl (3:1 v/v) in phosphate PAPR-type fertilizers

Sample No.	η_{PAPR}	P_2O_5 soluble in water [mg/100 cm^3]	P_2O_5 soluble in HNO_3 + HCl [mg/100 cm^3]
1	0.1	0.318	3.031
2	0.2	0.678	2.782
3	0.3	1.035	2.788
4	0.4	1.346	2.651
5	0.5	1.645	2.409

Water soluble phosphorus was measured using spectrophotometry method with vanadate-molybdate complex in water phase, while the total phosphorus was determined through the initial mineralization of fertilizer preparations using a mixture of nitric and hydrochloric acids in a volume ratio of 3: 1, and then by spectrophotometry method [15, 16]. The resulting coefficients were related to varying degrees of PAPR stoichiometric norm.

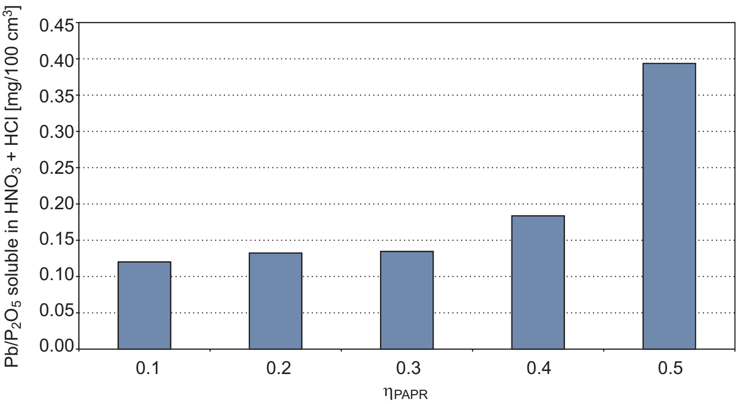

Fig. 2. Comparison of the content ratio of lead to phosphorus soluble in mixture of mineral acids HNO_3 + HCl (3:1 v/v) [$\alpha = Pb/P_2O_5$ (μg/g)/(mg/100 cm^3)] in relation to various degree of PAPR stoichiometric norm

The coefficient based on the analysis of content ratio of lead to phosphorus soluble in mixture of mineral acids HNO_3 + HCl (3:1 v/v) (Fig. 2) represent the raising trend with increased η_{PAPR} values and lead concentration contained in the PAPR-type fertilizers. Lead comes in this case mainly from phosphoric raw material, phosphate rock ZIN. The small contamination of samples with used reagents is also observed, these are vestigial amounts of lead inserted with the reagent. For coefficient based on the analysis of content ratio of lead to phosphorus soluble in water, the reverse trend is observed comparing to the total phosphorus. It is related with a fact that with increasing degree of PAPR stoichiometric norm the content of water soluble phosphorus also increases, that is phosphorus compounds available to plants and living organisms, but in the other hand the total content of phosphate decreases.

Conclusions

The results indicated that the highest lead content was found in an unprocessed ZIN (Israeli) phosphate rock which is caused by the ability of phosphate minerals to absorb this heavy metal. However, phosphate rock ZIN shows a very low content of lead compared to those from other regions of the world, such as phosphate rock from Pakistan with an average lead content of 89 μg/g or phosphate located in the South Africa-35 μg/g [17].

Partial acidulation of phosphate raw material by using less than stoichiometric amount of sulfuric acid allowed to obtain PAPR-type fertilizer formulations with lower lead content than the phosphate rock. Use of sulphuric acid in the analysis caused the transformation of organic lead compounds in the hard-absorbable sulphureous forms. In addition, the polarographic analysis has shown that with increasing degree of stoichiometric norm slightly increases the lead content in the investigated samples in relation to the quantity of total phosphorus.

The most preferred, due to the limited content of heavy metal toxicity, is the application of the lower η_{PAPR} values and using phosphate rocks with the smallest content of this heavy metal. The lead content in produced PAPR-type fertilizers is so low that when we use them for fertilization in temperate climate zone, for example for corn, which shows the greatest response to phosphorus fertilization, the content of lead per 1 ha of crop would be only 9.61 mg of Pb (using $\eta_{PAPR} = 0.1$) [18]. Therefore, fertilizers containing partially acidulated phosphate rocks are relatively competitive to other phosphate fertilizers. Their application may contribute to decrease in the level of lead content in agricultural soils, which has a beneficial effect on the microflora, microfauna, and reduce the potential risk to human health.

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BADANIE PRZYSWAJALNOŚCI OŁOWIU W PRODUKTACH ROZKŁADU SUROWCÓW FOSFOROWYCH TECHNIKĄ PAPR

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Abstrakt: Nawozy zawierające częściowo rozłożony fosforyt, czyli nawozy typu PAPR (z ang. *partially acidulated phosphate rock*) wykazują długotrwałe działanie dzięki zawartości fosforu o różnym stopniu rozpuszczalności. Ważna jest optymalizacja składu nawozów typu PAPR. Znajomość poziomu stężeń metali ciężkich w danym nawozie może się okazać kluczowa, jeśli chodzi o ekologiczne i zdrowotne aspekty wykorzystywania nawozów fosforowych częściowo rozłożonych. W badaniach zastosowano produkty typu PAPR otrzymane w warunkach laboratoryjnych poprzez roztwarzanie fosforytów z niestechiometryczną ilością kwasu siarkowego. Następnie przeprowadzano mineralizację uzyskanych nawozów w celu oznaczenia stężenia ołowiu. Zawartość ołowiu w nawozach typu PAPR badano za pomocą urządzenia Autolab metodą woltamperometrii pulsowej różnicowej.

Słowa kluczowe: fosforyty częściowo rozłożone, metale ciężkie, ołów, woltamperometria

DOI: 10.2428/ecea.2013.20(04)053 ECOL CHEM ENG A. 2013;20(4-5):565-572

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INVASIVENESS AND THE MORPHOMETRY OF *Steinernema feltiae* FROM DIFFERENT AGROCOENOSES OF POLAND

INWAZYJNOŚĆ I MORFOMETRIA *Steinernema feltiae* Z RÓŻNYCH AGROCENOZ POLSKI

Abstract: The paper presents the results of a study on the effect of environmental lead pollution on the invasiveness of nematodes obtained from the field. Study area included the vicinity of Czluchow, Mragowo, Rataje and Slupsk. The nematode *Steinernema feltiae* and larvae of the last growth stage of the greater wax moth *Galleria mellonella* L. were the study material. Nematodes were isolated from soil under laboratory conditions using Bedding and Akhurst's (1975) method. Physical and chemical analyses of soil samples were made in the Analytical Centre of the Warsaw University of Life Sciences. The total lead content was analysed with the flame atomic absorption spectrophotometry and soil pH with the potentiometric method acc. to the pB procedure (2 ed. of 21. June 2005). *Steinernema feltiae* were determined based on keys for entomopathogenic nematodes. The invasiveness of nematodes originating from studied agrocoenoses of Poland was evaluated.

Keywords: entomopathogenic nematodes, *Steinernema feltiae*, *Galleria mellonella*, heavy metals, lead ions

The activity of soil entomopathogenic nematodes depends on many environmental factors. Soil structure, soil temperature and moisture affect nematode biology [1]. These effects might be favourable or harmful.

The mechanical composition of soil is one of the factors affecting nematode survival and mobility. It was shown that the invasive larvae of entomopathogenic nematodes faster and easier penetrated insect's body in sandy or sandy-loamy substrate and just in such soils larval survival was the highest [2].

Invasive larvae of nematodes are able to actively search, infect and kill the host insect and to stay long in soil under favourable conditions. Nematodes are characterized by a high reproductive potential, broad food spectrum and the ability to produce dormant stages in a form of invasive larvae.

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Entomopathogenic nematodes living wild are a positive alternative to chemical means used in plant protection against pests. Introduction of biological methods to plant protection is a good way of limiting chemical insecticides. The selection of most effective breeds of entomopathogenic nematodes as bioinsecticide requires the knowledge of local communities of entomofauna (including plant pests) but also the communities of entomopathogenic nematodes living wild in a given habitat. It is probable that the effectiveness might be ensured by using the breeds taken from local nematode populations which are best fit to local conditions.

Soil dwelled by entomopathogenic nematodes is a habitat for other organisms and contains chemical compounds limiting nematode density. One of such limiting factors is lead, whose negative effect on entomopathogenic nematodes was demonstrated in many studies. Both lead and nematodes gather in the upper soil layers. Lead accumulates there and is not washed out downwards. Therefore, its harmful impact may last for years [3–8]. Harmful effect of lead(II) ions on entomopathogenic nematodes manifests itself not only during a direct contact of nematode larvae but also in the next generations [3, 6, 9]. Soil pH is another factor affecting nematode survival and mobility, largely decides upon the bioavailability and mobility of heavy metals. Natural acidification associated with the presence of carbon dioxide in the air prevails in the soils of Poland. This gas when dissolved in rain waters forms weak carbonic acid which falls to the soil with atmospheric precipitation. Optimum for biological processes of plants and soil organisms is pH in the range 5.5–7.2 [10, 11]. It was shown that pH values between 4 and 8 do not vary in their effect on nematodes but at pH 10 survival declines rapidly [10, 12].

Studies carried out on the entomopathogenic nematode-host insect system indicate that multiple infection of insects of a given species results in selection of a specific nematode race which is more pathogenic than the initial race [13, 14]. This may suggest that local populations of entomopathogenic nematodes differentiate under the effect of a characteristic species composition and domination structure of local insect communities [15].

New nematode species and places of their occurrence are being found worldwide [16–21]. Poland is the country, where faunistic studies are scarce.

This paper presents new sites of entomopathogenic nematodes in Poland and the degree of invasiveness of nematodes from the field.

Material and methods

Studies were carried out in the summer seasons of the years 2009–2010. Fifty soil samples were collected from 4 study areas (Fig. 1) of similar ecosystems (arable fields – spring cereals) in Poland in order to confirm the occurrence and to isolate entomopathogenic nematodes. Samples were collected with the Egner's sampler (diameter 2.5 cm) to the soil depth of 25 cm on uniform surfaces and in regular sampling grid. The method ensures complete and even sampling which allows obtaining of nematode densities in the soil.

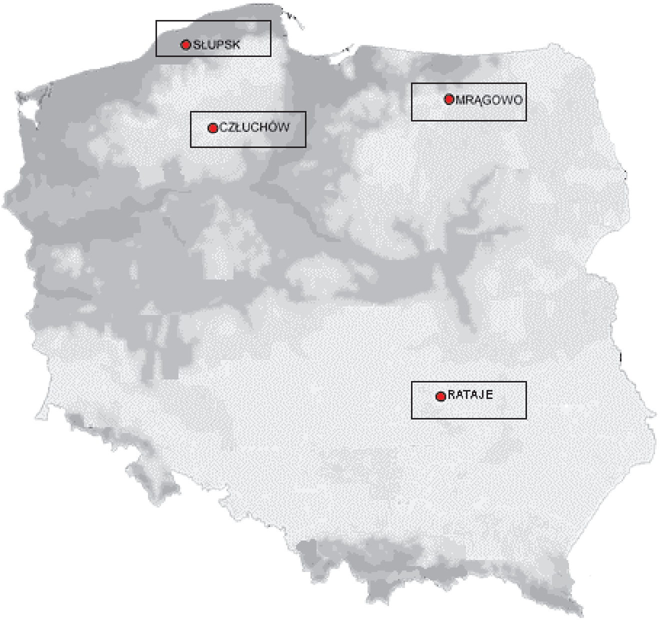

Fig. 1. Selected sampling sites

Physical and chemical soil properties were analysed in the Analytical Centre of the Warsaw University of Life Sciences. Concentration of total lead in soil samples was determined with the flame atomic absorption spectrophotometry, soil pH – with the potentiometric method acc. to the procedure pB (2nd ed. of 21st June 2005), and grain size structure.

Nematodes were isolated from soil samples in the lab with the Bedding and Akhurst's (1975) method [22, 23]. Well mixed soil samples were placed in plastic boxes of a volume of 250 cm^3 together with two trap insects (caterpillars of *G. mellonella*) from own laboratory culture. Samples were placed in a thermostat for 16 days at 20 °C. Every two days dead insects were removed from boxes and the reason of their death was estimated. Insects infected by nematodes were transferred to White's trap (1927) [24], to obtain invasive larvae of the nematode migrating from the insect's body. New live caterpillars of *G. mellonella* replaced dead insects in boxes. Nematode larvae obtained this way were used to infect the next caterpillars of *G. mellonella* (of a mean body weight of 0.165 g) to determine the invasiveness and to measure selected body sizes of the studied nematodes. Infective juveniles between 2 and 3 weeks old after their emergence from host cadavers were used. Control sample consisted of nematodes *S. feltiae* obtained from biological preparation "Owinema". The initial dose was 50 nematode larvae per insect. This is an optimum dose for obtaining maximum number of nematode larvae leaving the insect's body [25]. Nematode invasiveness was estimated based on the extensity and intensity of invasion. The experiment was repeated twice.

Results and discussion

Results of physical and chemical analyses of soil properties showed a natural lead content ranging from 11.88 to 21.7 mg/kg and soil pH from moderately to weakly acidic. Grain size structure of analysed soil samples was typical for sandy loam, sandy dust and light loam (Table 1).

Table 1

Results of analyses of soil samples

Site	Czluchow	Mragowo	Rataje	Slupsk
Longitude	17°23′16″	21°10′36″	21°00′41″	16°55′15″
Latitude	53°39′31″	53°55′23″	51°03′33″	54°26′16″
Pb [mg/kg]	11.88	11.91	13.6	21.7
pH	6.14	5.73	5.38	6.62
Grain size structure	sandy loam	sandy loam	sandy dust	light loam

Analyses of collected soil samples revealed the presence of entomopathogenic nematodes.

Based on keys for species determination, the nematodes isolated from soil samples were identified as *S. feltiae*. Measured body sizes and respective standards given by the authors of the species are given in Tables 2–4 [26].

Table 2

Analysed nematode larvae [μm]

Analysed samples	Control sample	*S. feltiae* from Czluchow	*S. feltiae* from Mragowo	*S. feltiae* from Rataje	*S. feltiae* from Slupsk	Standard size given in the literature
Mean body length	901	899	915	920	837	766–928
Mean body width	27	27	28	31	26	26–32

Table 3

Selected body sizes of the first generation female [μm]

Analysed samples	Control sample	*S. feltiae* from Czluchow	*S. feltiae* from Mragowo	*S. feltiae* from Rataje	*S. feltiae* from Slupsk	Standard size given in the literature
Mean body length	3377	3458	3506	3691	3214	3095–3774
Mean body width	199	190	211	242	186	170–254
Mean length of the pharynx	241	219	291	301	201	197–304
Mean tail length	59	52	65	68	49	39–70

Table 4

Selected body sizes of the first generation male [µm]

Analysed samples	Control sample	*S. feltiae* from Czluchow	*S. feltiae* from Mragowo	*S. feltiae* from Rataje	*S. feltiae* from Slupsk	Standard size given in the literature
Mean body length	1688	1531	1705	1798	1440	1414–1817
Mean body width	149	130	156	160	123	121–162
Mean length of the pharynx	134	133	136	138	133	164–180
Mean tail length	40	38	42	43	37	37–43
Mean length of spicule	66	65	67	67	63	62–68

The extensity of invasion in nematodes from various sites was similar among groups being, however, lower than that in the control sample. The lowest extensity (70 %) was noted in nematodes from the soil sample of the highest lead concentration (Slupsk). Nematodes from the three other sites (Czluchow, Mragowo, Rataje) had slightly higher extensity of invasion (Table 5, Fig. 2). These habitats showed similar soil pH and lead content.

Table 5

Invasiveness of studied nematodes

Analysed samples	Control sample	*S. feltiae* from Czluchow	*S. feltiae* from Mragowo	*S. feltiae* from Rataje	*S. feltiae* from Slupsk
Insect mortality [%]	100	98	98	98	97
Extensity of invasion [%]	100	78	72	83	70
Intensity of invasion [ind.]	22	15	13	17	10

The invasiveness of nematodes from agrocoenoses situated in various regions of Poland was lower than that in the control sample. There were also differences in the

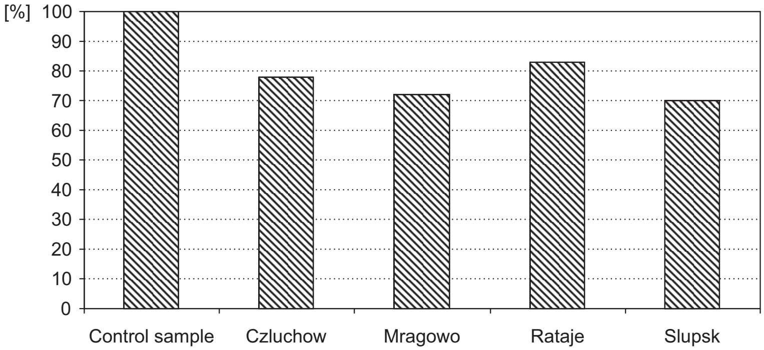

Fig. 2. Extensity of invasion of *S. feltiae* from studied sites in comparison with the control sample [%]

invasiveness between studied samples. The highest intensity (17 ind. of nematodes per insect) was found in nematodes from the vicinity of Rataje. The lowest intensity of invasion was characteristic for nematodes from near Slupsk (Table 5, Fig. 3).

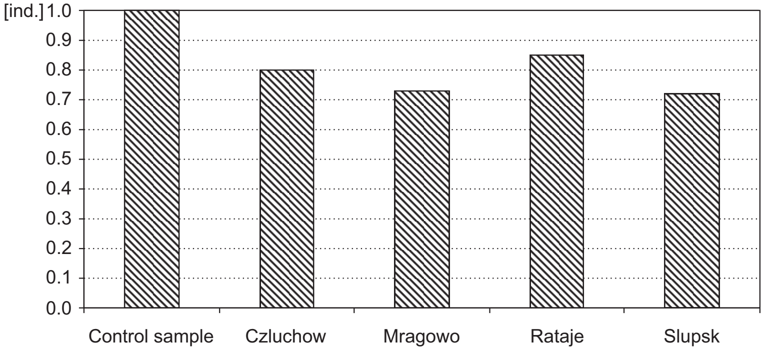

Fig. 3. The intensity of invasion of *S. feltiae* from studied sites in comparison with the control sample [ind.]

One-way ANOVA and the LSD test for the intensity of invasion showed highly significant differences between the control group and all field populations of nematodes. Highly significant differences in the intensity of invasion were also found between nematodes from Czluchow and Slupsk, Mragowo and Rataje, Mragowo and Slupsk and between nematodes from Rataje and Slupsk. No differences were noted between nematodes from Czluchow and Rataje. This result may evidence that populations from the same agrocoenoses situated in various regions of the country and characterised by different, though natural, concentrations of lead and soil pH from moderately to weakly acidic may show different degree of invasiveness. Similar results were observed in former studies made by the author in other localities of the country. Obtained results are also confirmed in studies by other authors who demonstrated that natural concentrations of heavy metals in soils were not the reason of nematode mortality but decreased their invasiveness [5].

Research on the biological activity of nematodes from the habitat are still under development. Scientific data suggest that the selection of indigenous breeds of nematodes is more beneficial than the use of commercial preparations based on nematodes. Such investigations are carries out in many countries around the world, including Hungary [27, 28]. In Poland, however, lack of detailed studies of biogeographical data, a collection of useful species and breeds entomopathogenic nematodes effectively limiting the populations of harmful insects.

Is important to continue and extend the research topic, which in future will enable better use of biological methods of plant protection.

Acknowledgement

The paper was financed in the years 2007–2010 as a research project from scientific funds.

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INWAZYJNOŚĆ I MORFOMETRIA *Steinernema feltiae* Z RÓŻNYCH AGROCENOZ POLSKI

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Abstrakt: W pracy przedstawiono wyniki badań nad wpływem zanieczyszczenia środowiska ołowiem na inwazyjność nicieni pozyskanych z terenu. Tereny badawcze obejmowały okolice miejscowości: Człuchów, Mrągowo, Rataje, Słupsk. Materiał do badań stanowiły nicienie *Steinernema feltiae* oraz larwy ostatniego stadium barciaka większego (*Galleria mellonella* L.). Nicienie wyizolowano z próbek glebowych w warunkach laboratoryjnych, metodą Beddinga i Akhursta (1975). Próbki glebowe zostały zbadane pod względem fizykochemicznym w Centrum Analitycznym SGGW. Oznaczono całkowitą zawartość ołowiu w glebie metodą płomieniowej absorpcyjnej spektrometrii atomowej FAAS oraz odczyn gleby metodą potencjometryczną, (wg procedury pB 14, wyd. 2 z 21.06.2005 r.).

Steinernema feltiae oznaczono na podstawie kluczy do oznaczania gatunku nicieni entomopatogenicznych. Oceniono inwazyjność nicieni pochodzących z badanych agrocenoz Polski.

Słowa kluczowe: nicienie entomopatogeniczne, *Steinernema feltiae*, *Galleria mellonella*, metale ciężkie, jony ołowiu

DOI: 10.2428/ecea.2013.20(04)054 ECOL CHEM ENG A. 2013;20(4-5):573-583

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CONTENT OF MERCURY AND CADMIUM IN THE STREAM OF SPENT ZINC-CARBON BATTERIES

ZAWARTOŚĆ RTĘCI I KADMU W STRUMIENIU ZUŻYTYCH BATERII CYNKOWO-WĘGLOWYCH

Abstract: According to EU Directive 2006/66/EC it is prohibited to sale batteries and accumulators containing more than 0.0005 wt. % mercury by weight and 0.002 wt. % of cadmium (except for special purpose batteries and button cells, in which the content of mercury should not exceed 2 % by weight).

In the stream of zinc-carbon batteries reaching the Polish market (and later the processing plants) one can find a large number of such that do not have information about the content of mercury and cadmium. The quantitative study of these two types of metals in particular parts of the zinc-carbon batteries type R6, standard AA, and in the stream of spent zinc-carbon batteries for recycling was described.

Obtained results are showing that overall cadmium content in individual elements of tested batteries, referenced to the total weight of the battery does not exceed the value permissible by the EU Directive in the amount of 0.002 % by weight of Cd in each of the analyzed batteries. However, the overall mercury content in individual parts of tested batteries for three of them exceeds the value permissible by the EU Directive (Directive 2006/66/EC, 2006), showing the amount of 0.0005 % of Hg by weight.

Keywords: zinc-carbon batteries, mercury, cadmium

Introduction

In accordance with the Directive on batteries and accumulators and their waste [1], all EU member states were obliged to reach 50 % recycling rate for the batteries used by end users until 26 September 2010. In addition, the provision to reach 65 % recycling rate for lead-acid accumulators and 75 % recycling rate for nickel-cadmium accumulators was also imposed.

This directive, in force in the EU since 26 September 2006 has also established the minimum waste battery collection rates amounting to 25 % until 26 September 2012

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and 45 % until 26 September 2016. In order to achieve these levels the producers of batteries and accumulators will have to bear the costs of collecting, processing and recycling of waste batteries and the costs of implementing a campaign to increase public awareness.

At the same time this Directive prohibits the sale of batteries and accumulators containing more than 0.0005 wt. % mercury and 0.002 wt. % of cadmium (except for special purpose batteries and button cells, in which the content of mercury should not exceed 2 % by weight).

In the stream of zinc-carbon batteries reaching the Polish market (and later the processing plants) there is a large number of those for which the information on the content of mercury and cadmium is not specified. Due to this situation companies dealing with pyro- and hydrometallurgical methods of waste batteries recycling face substantial, technological problems while processing these wastes.

The quantitative study of these two types of metals in particular elements parts of the zinc-carbon batteries type R6, standard AA and in the stream of spent zinc-carbon batteries for recycling was described below.

Zinc-carbon batteries

Characteristics of zinc-carbon batteries

The construction of the battery as well as of its overall and material composition have been shaped quite a long time ago, therefore in this respect there should be no significant differences between the products of different producers – Table 1 [2].

Table 1

Material composition of zinc-carbonate batteries (Zn-C), % by weight, based on [2]

Constituent	Producer [%]	
	A	B
Paper	3.21	5.80
Steel	35.79	30.48
Plastic	2.66	2.87
Graphite rod	5.85	6.86
Powder	46.33	49.19
Humidity	4.93	1.50
The rest / residue	1.23	3.30

A metallic zinc (Zn) in the form of powder constitutes the anode, electrolytically manufactured manganese oxide (MnO_2), mixed with graphite to ensure good electrical conductivity, works as a cathode. The electrolyte is concentrated aqueous solution of ammonium chloride (NH_4Cl), to which the zinc oxide (ZnO) was added to prevent pulping of metallic zinc. These materials are placed in a nickel-plated steel container which is used as a cathode current collector. A cathode (in the external part) is separated from the anode (in the internal part) by the porous interlayer (paper/cellophane) enabling the free movement of ions. A tin-plated brass rod constitutes an anode current collector. The battery is closed by a steel cover, sealed with plastic polyamide and separated by a cardboard partition from the anode exit. A thin polyvinyl chloride sleeve constitutes an external battery cover.

Battery powder ("black battery mass") is the most valuable source of metals, therefore a number of publications related to its chemical composition, methods of processing and recovery of valuable components, mainly zinc and manganese can be found in the literature [2–5]. Comparison of the composition of the examined battery powders with the stream of spent zinc-carbon batteries (Zn-C) from different producers is presented in the Table 2.

Table 2

Comparison of chemical compositions, stated in the literature, of battery powders from the stream of spent zinc-carbon batteries (Zn-C) and/or zinc-manganese (Zn-Mn), in wt. %

Sources Metals [%]	E. Sayilgan et al [2]	T.-H. Kim et al [3]	G. Senanayake et al [4]	B. Ruffino et al [5]
Mn	26.60	23.9	22.7	24.1
Zn	13.24	14.9	20.8	21.3
Fe	1.58	4.00	2.56	1.09
Cr	< 0.0028	—	—	—
Al	0.44	—	—	—
K	0.15	—	—	0.97
Cl	4.26	—	—	—
Ti	0.01	—	—	—
Si	1.35	—	—	—
Na	—	—	—	—
Hg	**—**	**—**	**< 0.1**	**—**
Pb	—	—	< 0.1	—
Ni	—	—	< 0.1	0.118
Cd	**—**	**—**	**—**	**0.033**
Co	—	—	< 0.1	< 0.001
Cu	—	—	< 0.1	—

Nearly all examined "black battery masses" contain mercury and cadmium in an amount from a few to several milligrams per kilogram of fraction. The confirmation of this situation are the results of the research included in J.A. Guevara-Garcia and V. Montiel-Corona works [6], where the authors examined battery powders from different producers of Zn-C batteries type R6 standard AA (Duracell, Eveready, Kodak, Heavy duty, Panasonic, Power cel, Glip 2000, Tectron, Rocket) and demonstrated that all of them include in their composition Hg and Cd in the amount from 0.31 ± 0.01 to 0.88 ± 0.02 wt. % Hg and from 0.11 ± 0.06 to 0.68 ± 0.31 wt. % Cd – Table 3.

Table 3

The content of mercury and cadmium in a black mass of Zn-C battery made by different producers, in wt. %, based on [6]

Producer	Hg [%]	Cd [%]
Duracell	0.58 ± 0.03	0.17 ± 0.07
Eveready	0.31 ± 0.01	0.30 ± 0.02
Kodak	0.84 ± 0.01	0.46 ± 0.12
Heavy duty	0.88 ± 0.02	0.11 ± 0.06
Panasonic	0.65 ± 0.02	0.68 ± 0.31
Power cell	0.62 ± 0.03	0.32 ± 0.07
Glip 2000	0.64 ± 0.02	0.46 ± 0.34
Tecton	0.51 ± 0.01	0.32 ± 0.14
Rocket	0.60 ± 0.03	0.47 ± 0.071

As for the other components of spent Zn-C batteries type R6 standard AA (fractions other than "black battery mass"), it is difficult to find information about their chemical composition; only the authors [5] carefully examined the remaining fraction after mechanical separation of the cathode mass, specifying its composition – Table 4.

Table 4

Composition of fraction other than "black battery mass" after mechanical processing of zinc-carbon batteries (Zn-C) type R6 standard AA, based on [5]

Metals	Zn-C batteries, R6 AA	Metals	Zn-C batteries, R6 AA
Na [mg/kg]	659	Zn [%]	21.8
K [%]	0.380	Ni [%]	0.004
Ca [%]	0.312	Cd [%]	0.004
Mg [mg/kg]	503	Cu [mg/kg]	20.0
Ba [mg/kg]	175	Cr [mg/kg]	19.0
Fe [%]	0.420	Pb [mg/kg]	708
Mn [%]	5.10	Co [%]	0.003

The number of zinc-carbon batteries reaching the Polish market

The stream of zinc-carbon batteries reaching the Polish market at the turn of 2002–2008 (diagram Fig. 1) changes significantly. In 2002, the amount of this type of batteries was over one hundred and forty million units, in 2003 and 2004 there was an increase to more than one hundred and seventy million, and since 2005 a drop in their share to 47 million units in 2008 could be observed. It is a result of launching the

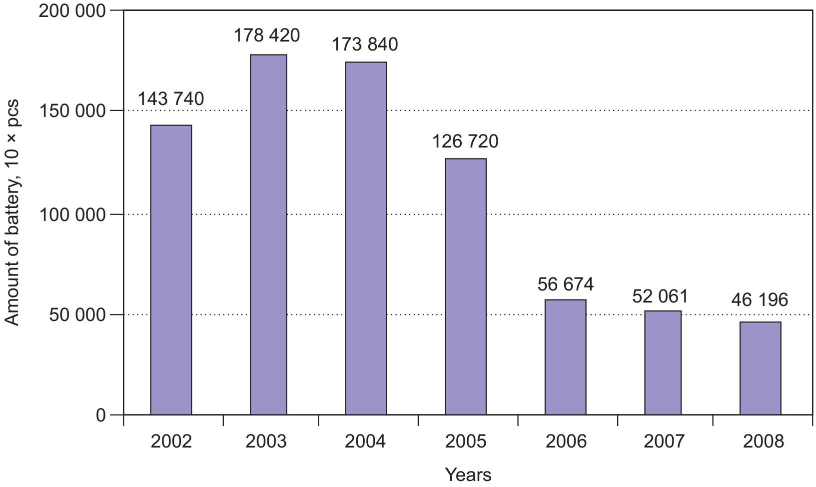

Fig. 1. The stream of zinc-carbon batteries reaching the Polish {market} in the years 2002–2008; data provided by the recovery organization REBA Organizacja Odzysku S.A. [7]

second type of batteries into sale – rechargeable batteries, which can be used by consumers for a longer period of time. However, it does not change the fact that the alkaline Zn-C battery type R6 (standard AA) still remains the most popular electrochemical source of energy on the market (not only in Poland). Undoubtedly this is related to the availability and low cost of components, good characteristics of battery life, relatively low toxicity of reagents, mass nature of production and consequently the price – a key criterion for the customer.

As a consequence these sources of energy dominate in the stream of batteries collected at the points of selective collection and acquired in the process of segregation.

Materials and methods

Tested material

The tested material consisted of spent zinc-carbon batteries type R6, standard AA (further referred to as B_1, B_2, B_3, B_4, B_5) of different producers, which declared on the label that the batteries do not contain cadmium and mercury (Cd, Hg "free").

Mechanical processing

The batteries were initially subjected to mechanical processing – separating into individual construction parts [8]: metallic collector +/– (Fig. 2), graphite collector (Fig. 3), steel or plastic casing (Fig. 4a, Fig. 4b), cathode mass (Fig. 5), zinc anode (Fig. 6), plastic spacer (Fig. 7), paper spacer (Fig. 8).

Subsequently, in order to determine the weight of the shares, the individual elements of the battery were weighted – Table 5, Figure 9. The average weight of tested batteries

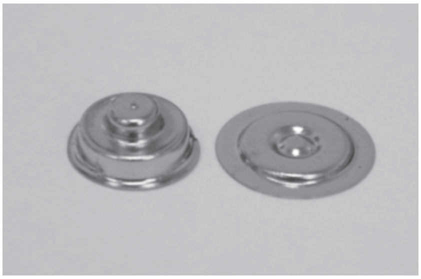

Fig. 2. Metallic collector +/- of Zn-C battery

Fig. 3. Graphite collector of Zn-C battery

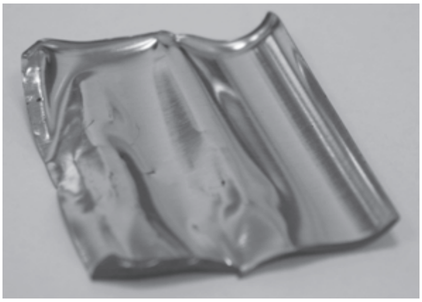

Fig. 4a. Steel casing of Zn-C battery

Fig. 4b. Plastic casing of Zn-C battery

Fig. 5. Cathode mass of Zn-C battery

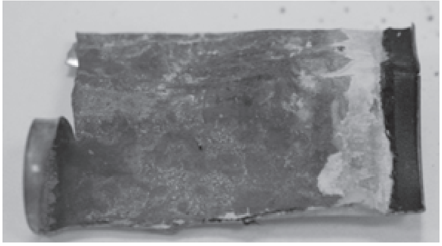

Fig. 6. Zinc anode of Zn-C battery

Fig. 7. Plastic spacer of Zn-C battery

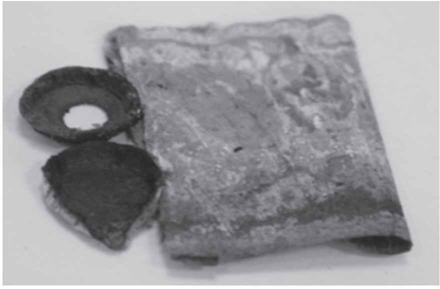

Fig. 8. Paper spacer of Zn-C battery

Table 5

Weight of individual elements of zinc-carbon batteries : B_1–B_5 [g]

Tested batteries	B_1	B_2	B_3	B_4	B_5
Size	AA				
Type	R6				
Construction elements [g]:					
Metallic contacts (+/–)	0.50	0.41	0.50	0.47	0.45
Graphite collector	1.00	0.30	1.17	1.07	1.17
Casing	3.32	0.15	3.34	3.32	2.99
Cathode mass	9.18	12.77	9.09	7.51	8.65
Zinc anode	2.08	0.42	2.34	4.09	2.35
Spacer:					
Plastic	0.50	0.39	0.47	0.45	0.49
Paper	0.44	0.28	0.36	0.55	0.62

was 17.0 g, and the cathode mass (the so-called "black battery masses") had the largest weight share, which accounted for an average of 56 % by weight of the whole battery.

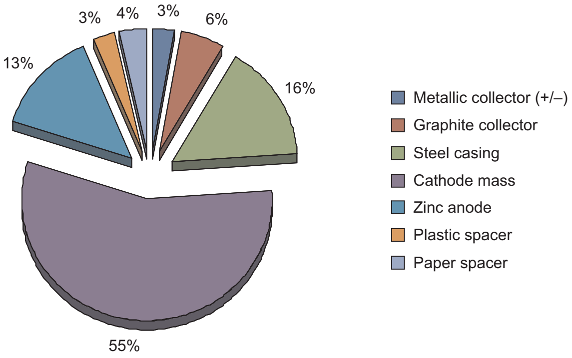

Fig. 9. The average percentage of the mass share of the construction components of zinc-carbon batteries [%]

Analytical methods

In the present study metals (Cd, Hg) were determined by atomic absorption spectroscopy, in accordance with the test procedures developed in the Laboratory of Toxicology and Environmental Research Institute of Environmental Protection Engineering, Wroclaw University of Technology.

Mercury was determined directly from samples without prior preparation of the sample (mineralization), using AMA 254 (Altec) instrument. It is an atomic absorption spectrometer using the technique of amalgamation, designed for determination of total mercury content, irrespective of the form of its occurrence, in liquid and solid samples.

Measurements were carried out at a wavelength of 254 nm. The limit for the determination of Hg was 0.03 ng.

Cadmium from solution was determined using GBC ΣAvanta 932 instrument, after microwave mineralization (Milestone instrument) of individual samples. The minimum detectable concentration of Cd was 0.0022 mg/dm^3.

Results

The content of cadmium and mercury in individual units of tested Zn-C batteries is shown in the Tables 6 and 7.

Table 6

The content of cadmium in individual parts of tested Zn-C batteries

Construction element	Cd [mg/kg]				
	Tested batteries				
	B_1	B_2	B_3	B_4	B_5
Metallic contacts (+/–)	[a] N/A	N/A	N/A	N/A	N/A
Graphite collector	N/A	N/A	N/A	1.5	2.8
Casing	N/A	N/A	N/A	3.6	N/A
Cathode mass	N/A	N/A	N/A	0.88	2.6
Zinc anode	4.4	11	11	2.9	8.0
Spacer:					
Plastic	N/A	4.6	0.80	0.79	N/A
Paper	8.7	N/A	N/A	0.60	1.3

[a] N/A – content of Cd below the detection limit of the method 0.32 mg/kg.

Table 7

The content of mercury in individual parts of tested Zn-C batteries

Construction element	Hg [mg/kg]				
	Tested batteries				
	B_1	B_2	B_3	B_4	B_5
Metallic contacts (+/–)	0.29	2.7	3.2	12	7.8
Graphite collector	5.8	12	8.7	14	150
Casing	33	4.0	1.9	15	31
Cathode mass	69	2400	950	220	8900
Zinc anode	19	77	120	25	160
Spacer:					
Plastic	24	36	18	40	11
Paper	19	54	71	62	330

The results obtained indicate that all tested batteries include in its parts mercury and cadmium in detectable concentrations – Fig. 10 and 11. However, the content of these two metals harmful to the environment and man differs significantly between batteries – Tables 6 and 7. The data in Table 6 show that only metallic contacts +/– of batteries do not contain cadmium (in amounts above the detection limit, in this case equal to 0.32 mg/kg), whereas it occurs in all zinc anodes in amount ranging from 8.0 mg/kg (B_5 battery) to 11 mg/kg (B_2 and B_3 batteries). In batteries B_4 and B_5 this element is a part of graphite collectors (B_4: 1,5 mg/kg, B_5: 2,8 mg/kg) and cathode masses (B_4: 0,88 mg/kg, B_5: 2,6 mg/kg). Also the plastic casing of B_4 battery contains Cd in the amount of 3.6 mg/kg. Plastic spacers used by four producers in manufacturing Zn-C batteries (B_2, B_3, B_4, B_5) contain cadmium in the amount of 0.80 (B_3) to 1.6 (B_2) mg/kg.

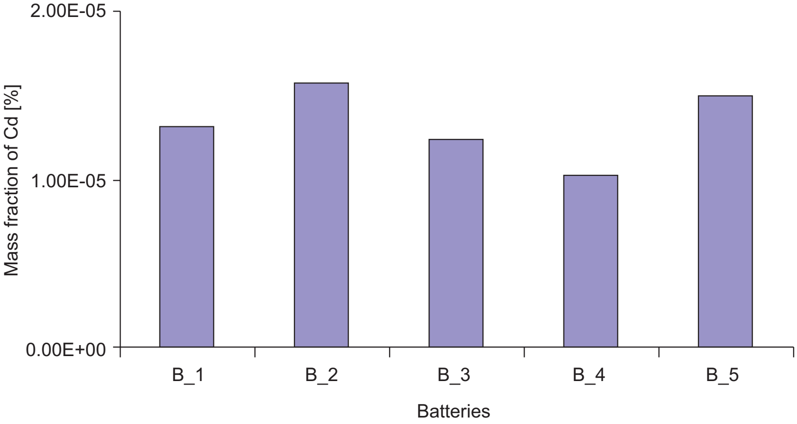

Fig. 10. Mass fraction of Cd in the tested batteries B_1–B_5 [%]

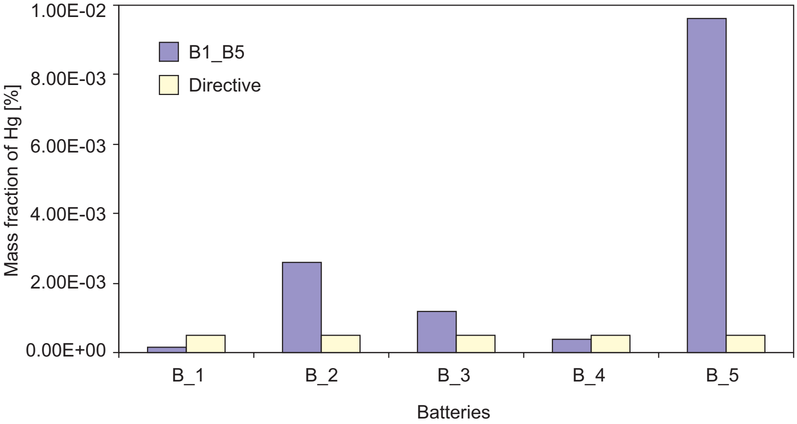

Fig. 11. Mass fraction of Hg in the tested batteries B_1 to B_5 [%]

All elements of tested batteries contain mercury – Table 7. The highest concentration of Hg was observed in cathode masses: from 69 mg/kg in battery B_1 to 2400 mg/kg in battery B_2 , to which mercury is added by producers to prevent the corrosion of zinc anodes during the battery life [8]. The lowest mercury concentration was observed in the metal contacts +/–, within the range of 2.9 mg/kg for battery B_1 to 12 mg/kg in battery B_4. In graphite collectors the content of mercury ranged from 58 mg/kg in battery B_1 to 150 mg/kg in battery B_5, as for casings where the lowest concentration was found in the case of battery B_3: 1.9 mg/kg, while the highest for the battery B_1: 33 mg/kg. The concentration of mercury in zinc anodes ranged from 19 mg/kg to 160 mg/kg (batteries B_1 and B_5). In spacers of the tested batteries the concentration of mercury is maintained at similar level in all cases (for all producers) and in average for plastic separators it amounts to 26 mg/kg, and for paper separators to 110 mg/kg.

Conclusions

1. The overall cadmium content in individual elements of tested batteries (B_1 to B_5) presented in the diagram Fig. 10, referenced to the total weight of the battery does not exceed the value permissible by the EU Directive as the amount of 0.002 % by weight of Cd in each of the analyzed batteries**.**

2. The overall mercury content in individual elements of tested batteries (B_1 to B_5) presented in the diagram Fig. 11, for three batteries (B_2, B_3 and B_5) exceeds the value permissible by the EU Directive [1] as the amount of 0.0005 % by weight of Hg (drastically in the case of batteries B_5), for two batteries it complies with the standard. The results of this studies indicate the need to verify Zn-C batteries, type R6 standard AA launched into the market in terms of mercury content prior to their admission to trading.

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ZAWARTOŚĆ RTĘCI I KADMU W STRUMIENIU ZUŻYTYCH BATERII CYNKOWO-WĘGLOWYCH

Wydział Inżynierii Środowiska
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Abstrakt: Dyrektywa unijna dotycząca baterii i akumulatorów oraz ich odpadów [1] zakazuje sprzedaży baterii i akumulatorów zawierających więcej niż 0,0005 % wagowych rtęci oraz 0,002 % kadmu (z wyjątkiem baterii specjalnego przeznaczenia i ogniw guzikowych, w których zawartość rtęci nie powinna przekroczyć 2 % wagowych). Jednak w strumieniu baterii cynkowo-węglowych trafiających na polski rynek (a później do zakładów przetwórczych) znajduje się duża ilość takich, na których nie ma informacji o zawartości rtęci i kadmu. Ten stan rzeczy powoduje, iż przedsiębiorstwa zajmujące się recyklingiem odpadów bateryjnych metodami piro-, jak i hydrometalurgicznymi mają problemy technologiczne podczas przeróbki tych odpadów. W pracy przedstawiono próbę oszacowania ilości tych dwóch metali w poszczególnych elementach baterii cynkowo-węglowych typu R6, standard AA oraz w strumieniu zużytych baterii cynkowo-węglowych trafiających do recyklingu.

Słowa kluczowe: baterie cynkowo-węglowe, rtęć, kadm

DOI: 10.2428/ecea.2013.20(04)055 ECOL CHEM ENG A. 2013;20(4-5):585-594

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MULTIVARIATE STATISTICAL INTERPRETATION OF CLINICAL DATA OF PROLACTINOMA PATIENTS

INTERPRETACJA STATYSTYCZNA WIELOWYMIAROWYCH DANYCH KLINICZNYCH PACJENTÓW Z PROLAKTYNEMIĄ

Abstract: This study reveals some specific relationships between the clinical parameters usually checked at prolactinoma patients allowing in such a way to optimize the monitoring procedure by selecting a reduced number of health status indicators. This is achieved by multivariate statistical interpretation of the parameter values where clusters of indicators with correlated (similar) response are proven. Additionally, four patterns of prolactinoma patients are found each one of them characterized by specific clinical indicators. This original information could be of use for better interpretation of the health status of the patients.

Keywords: prolactinoma, clinical data, data treatment, cluster analysis, principal components analysis

Introduction

Prolactinoma is a benign tumor (adenoma) of the pituitary gland which produces the hormone prolactin. Autopsy studies in the USA indicate that about 25 % of the citizens have small pituitary tumors and that about 40 % of them produce prolactin [1].

The cause of pituitary tumors remains unknown. It is established that stress can significantly raise the prolactin levels. This can make the stress a diagnostic parameter.

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At a very low number of patients the level of cortisol (a hormone associated with stress) is determined.

The prolactin has a broad spectrum of biological actions, which determine the metabolic control [2].

The symptoms caused by the hyperprolactinaemia are [2–4]: hypogonadotropic amenorrhea as a result of lowered *follicle-stimulating hormone* (FSH) levels; infertility; galactorrhea; loss of bone mass; hypogonadism; changes in the lipid metabolism.

The symptoms that are caused by the mass effect of the tumor upon the adjacent tissues are: Bitemporal hemianopsia (due to pressure on optic chiasma); vertigo; nausea, vomiting. Except availability of prolactinoma there are other reasons for moderate raise of the prolactin levels: the action of some medicines; existence of other pituitary tumors; pregnancy and lactation [5]. The prolactinoma medication has the aim to lower the prolactin secretion to the normal level, to correct visual impairments and to restore the normal function of the pituitary gland through lowering the size of the tumor. The dopamine suppresses the size of the tumor and lowers the prolactin levels at about 80 % of the patients [6].

When the medication can not be well tolerated or failed to reduce the prolactin levels the restoration of the normal pituitary function can be made through operative elimination of the tumor [7]. Depending on the size of the tumor and how much of it is removed, studies show that in 20 to 50 % of patients it will recur, usually within five years [8].

There are no studies trying to interpret in a multivariate way clinical data from prolactinoma patients.The aim of the present study is to detect specific relationships between the medical indicators measured for prolactinoma patients and to find various patterns of similarity between the patients included in the group of observation. The information extracted will help in the optimization of the testing of the patients (*eg* reducing the number of observed parameters) or in finding discriminating medical indicators for formation of different groups (patterns) of patients with similar medical status.

Experimental

Clinical analysis

The data of forty six patients of the Clinic of Endocrinology, Medical University of Sofia are included. Thirty nine of them are women and seven are men.

The next clinical parameters are used for the multivariate statistical analysis:

1. BMI, body mass index, kg/m^2.
2. ESR, *Erythrocyte sedimentation rate* – the rate of the sedimentation of erythrocytes for a period of 1 hr. The reference values: up to 25 mm/h for women under 50 years and up to 30 mm/h for women over 50 years, up to 18 mm/h for men under 50 years and up to 22 mm/h for men over 50.
3. HGB, *haemoglobin*, reference values for women 120–160 g/dm^3 and for men 135–180 g/dm^3.

4. RBC, *red blood cells* is a blood test, which presents the number of erythrocytes. Reference values for women (3.7–5.3) · 10^{12}/dm^3 and for men (4.4–5.9) · 10^{12}/dm^3.

5. PLT, *platelits*, reference values (130–360) · 10^9/dm^3.

6. Alb, *Albumin*. Serum albumin is the main component of the blood plasma. Reference values for Alb: 35–53 g/dm^3.

7. Glu, *Glucose*. The levels of the blood glucose are 2.8–6.1 mmol/dm^3.

8. Chol, *Cholesterol*, reference values 3.4–5.2 mmol/dm^3.

9. LDL, *Low Density Lipoproteins*, reference values 2.6–3.2 mmol/dm^3.

10. Trigl, *Triglycerides*, reference values 0.6–1.7 mmol/dm^3.

11. ALAT, *alanine aminotransferase* – catalyses two reactions of the alanine. This enzyme is a clinical index of the liver's status. Reference values 5–40 U/dm^3.

12. CK, *Creatine kinase* or CPK, *Creatine phosphokinase* is the enzyme, which catalyses the conversion of creatine into phosphocreatine with *adenosine triphosphate*, ATP. Reference values for women 20–180 U/dm^3 and for men 30–200 U/dm^3.

13. Prol, *Prolactin* is a hormone - glycoprotein secreted from the front lobe of the pituitary gland. It supports the production of the estrogens and progesterone. Prolactin stimulates the milk production. Reference values for women 59.3–619.0 mIU/dm^3 and for men 44.5–375.2 mIU/dm^3.

14. FSH, *Follicle-stimulating hormone* is a glycoprotein hormone. It is synthesized and secreted from the front lobe of the pituitary (adenohypophysis). Reference values for women (follicular phase) 2.5–10.2 U/dm^3 and for men 1.4–18.1 U/dm^3.

15. Cortisol is a steroid hormone secreted from the adrenal glands. It is regulated from the pituitary gland. Its level is the most raised at 8 h in the morning with reference values 118.2–618 nmol/dm^3. The cortisol level is raised after physical and emotional stress and provokes decomposition of proteins and fats.

Multivariate statistical methods

In the present study *Cluster analysis* (CA) and *Principal Components Analysis* (PCA) were used.

Cluster analysis is well-known and widely used multivariate statistical approach [9]. In order to cluster objects characterized by a set of variables (*eg* patients by clinical parameters), one has to determine their similarity. A preliminary step of data scaling is necessary (*eg* autoscaling or z – transform) where normalized dimensionless numbers replaces the real raw data values. Thus, even serious differences in absolute values are scaled to similar ranges. Then, the similarity or the distance between the objects in the variable space can be determined usually by calculation of the Euclidean distance. There is a wide variability of clustering (linkage) algorithms but the typical ones include the single linkage, the average linkage or the Ward's method. The representation of the results of the cluster analysis is performed by a tree-like scheme called dendrogram.

Principal components analysis (PCA) [9] is a typical display method, which allows to estimate the internal relations in the data set. There are different variants of PCA but basically, their common feature is that they produce linear combination of the original columns in the data matrix (data set) responsible for the description of the variables characterizing the objects of observation. These linear combinations represent a type of abstract measurements (factors, principal components) being better descriptors of the data structure (data pattern) than the original (chemical or physical) measurements. Usually, the new abstract variables are called latent factors and they differ from the original ones named manifest variables. It is a common finding that just a few of the latent variables account for a large part of the data set variation. Thus, the data structure in a reduced space can be observed and studied.

Results and discussion

Cluster analysis of 15 variables (clinical parameters) and 46 objects (patients)

In Fig. 1 the dendrogram for the clustering of 15 clinical parameters measured on 46 prolactinoma patients is shown. The clustering was performed after z-transformation of the raw data using the squared Euclidean distance as similarity measure and the Ward's method of linkage.

Six clusters are formed:

- – K1: CORT, ALB, PLT – "blood damaging factor";
- – K2: RBC, HGB – "blood oxidation factor";
- – K3: LDL, CHOL – "health quality factor";
- – K4: FSH, ESR – "blood sedimentation factor";
- – K5: CK, ALAT – "enzyme factor";
- – K6: TRIGL, GLU, BMI – "metabolic syndrome factor".

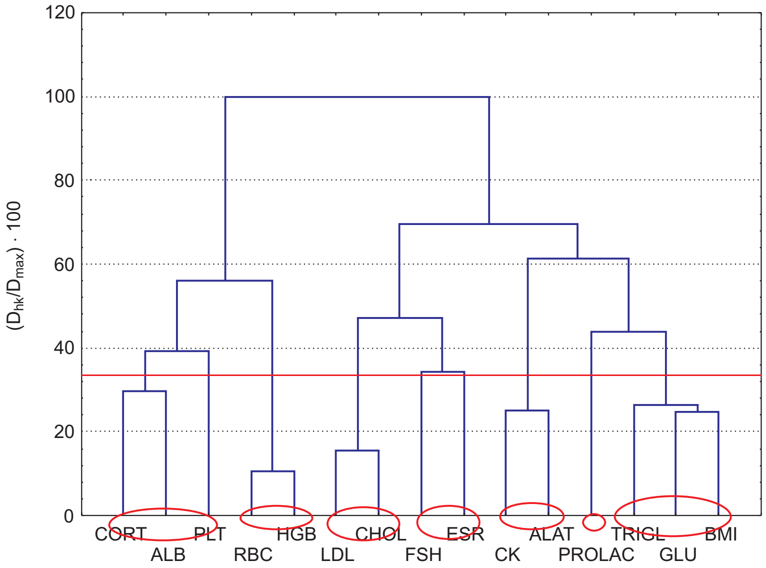

Fig. 1. Hierarchical dendrogram for 15 medical parameters with 46 patients

The parameter “PROLAC” is rather an outlier (“prolactin factor”).

It could be concluded that 6–7 parameters are good enough to characterize the status of the patients (at least one from each group).

Principal Components Analysis

These results are confirmed by the application of principal components analysis (PCA) to the same data set. The input data ere again standardized and the Varimax rotation procedure was applied to the data set. In Table 1 the factor loadings for 6 latent factors are shown.

Table 1

Factor loadings (statistically significant loadings are marked, 46 patients)

Parameter	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6
BMI	0.11	**0.68**	0.04	–0.15	–0.13	–0.59
ESR	**0.77**	0.11	0.10	0.08	–0.02	–0.21
HGB	**–0.85**	0.04	–0.18	0.05	0.11	–0.07
RBC	**–0.85**	0.14	0.03	0.18	0.02	–0.06
PLT	0.001	–0.06	0.20	0.10	**0.79**	–0.00
ALB	–0.17	–0.02	–0.29	–0.20	**0.74**	0.04
GLU	–0.08	**0.80**	–0.16	0.23	0.08	–0.02
CHOL	0.35	0.37	**0.60**	0.05	0.09	0.37
LDL	0.21	–0.07	**0.76**	–0.13	0.29	0.26
TRIGL	–0.07	**0.74**	0.27	–0.27	–0.16	0.11
ALAT	0.00	0.14	0.11	**–0.79**	0.07	0.08
CK	0.29	0.02	–0.07	**–0.75**	–0.13	0.11
PROLAC	0.06	–0.01	–0.11	0.09	0.00	**–0.88**
FSH	0.19	0.32	–0.05	**0.64**	–0.18	0.32
CORT	0.01	–0.01	**–0.84**	0.01	0.22	0.13
Expl. var. %	15.9	13.0	13.0	12.4	10.2	9.5

Again, 6 latent factors are responsible for the data structure. One could easily find the correlations shown by cluster analysis:

– *“Blood oxidation factor”* (explanation of nearly 16 % of the total variance) with high loadings for HGB and RBC being negatively correlated to ESR;

– “*Metabolic syndrome factor”* (13 % of the total variance) indicates the correlation between TRIGL, GLU and BMI;

– *“Health quality factor”* (13 % of the total variance) shows the relationship between CHOL and LDL (both parameters are negatively correlated to CORT)

– *“Enzyme factor”* (over 12 % explanation of the total variance) reflects the correlated impact of both enzymes (negative correlated to FSH hormone);

– *“Blood damaging factor”* confirms the correlation between PLT and ALB (10.2 % of the total variance) in this case, however, not correlated to CORT. It might mean that CORT is playing an independent role in the whole scheme of variables impact on the medical status.

– *“Prolactin factor”* is an independent factor (outlier) with significant contribution to the total variance of the system (over 9 %). Its specific position is indication for its discriminating ability among the group of patients.

In Fig. 2 the clustering of the objects of interest (46 patients) is indicated. Four major clusters are formed. It is obvious that patient 41 is a typical outlier. Indeed, the prolactin value measured for this particular patient is far above the values of the rest of patients (13340 units; all others are between 200 and 1200). The presence of an outlier could seriously deteriorate the data mining scheme and bring wrong conclusions about the role of different discriminating parameters in the formation of the four groups (patterns) of prolactinoma patients. That is why it is recommendable to eliminate the object from the statistical analysis. Of course, it is an important task to screen further this particular patient. Thus, is will become possible to better understand why he (the patient is one of the few male patients in the group) shows such high level of prolactin.

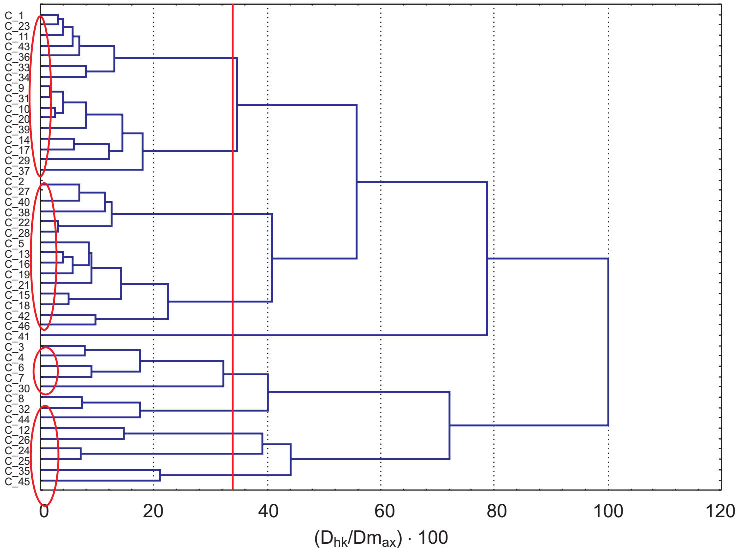

Fig. 2. Hierarchical dendrogram for 46 patients with 15 medical parameters

After elimination of the outlying object the multivariate statistical procedure for data mining was applied again.

There is no change of the clustering of the medical parameters after elimination of the outlier from the data set (Fig. 3). One could readily see the six groups being identical with those in Fig. 1 and the specific position of PROLAC.

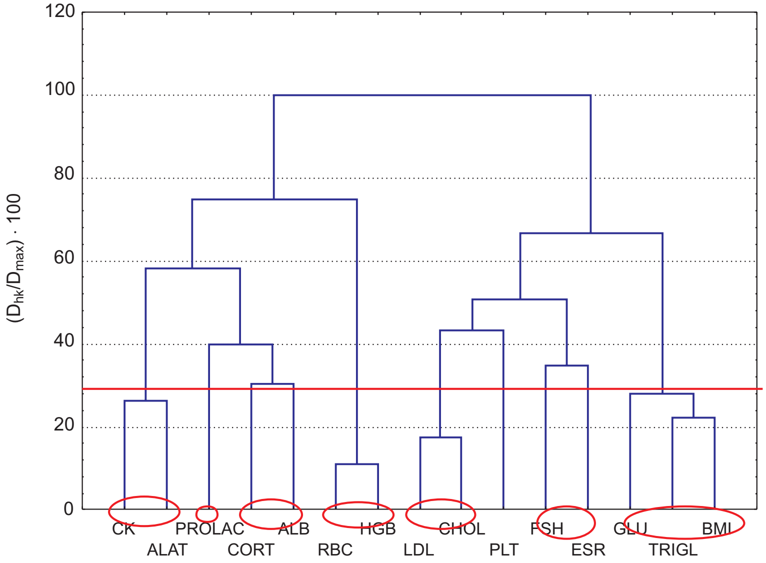

Fig. 3. Hierarchical dendrogram for 15 medical parameters with 45 patients

The same results are obtained by interpretation of the factor loadings from PCA. Again, six latent factors are responsible for the data structure and explain nearly 70 % of the total variance (Table 2).

Table 2

Factor loadings (statistically significant loadings are marked, 45 patients)

Variable	PC-1	PC-2	PC-3	PC-4	PC-5	PC-6
BMI	0.11	**0.82**	–0.00	0.14	–0.13	–0.11
ESR	**0.72**	0.18	–0.14	–0.17	–0.02	0.20
HGB	**–0.86**	0.06	0.20	–0.02	0.14	0.06
RBC	**–0.89**	0.12	–0.00	–0.16	0.02	0.05
PLT	–0.00	–0.17	–0.28	–0.01	**0.73**	–0.25
ALB	–0.17	0.02	0.20	0.17	**0.77**	0.18
GLU	–0.08	**0.68**	0.15	–0.29	0.15	–0.25
CHOL	0.30	0.38	**–0.71**	–0.19	0.06	0.06
LDL	0.16	–0.07	**–0.86**	0.09	0.20	0.12
TRIGL	–0.09	**0.76**	–0.28	0.13	–0.13	0.01
ALAT	0.09	0.21	–0.06	**0.82**	0.06	–0.19
CK	0.30	0.20	0.03	**0.59**	–0.09	0.50
PROLAC	–0.01	–0.31	0.00	0.01	0.01	**0.83**
FSH	0.16	0.21	0.01	**–0.72**	–0.12	–0.14
CORT	0.02	–0.02	**0.70**	–0.11	0.37	0.26
Expl. var. %	15.7	14.9	13.5	12.3	9.6	8.7

The most serious difference to the previous case with 46 patients is to be expected in the clustering of the objects (patients) after elimination of the outlier with extremely high value of prolactin.

In Fig. 4 the clustering of the 45 patients is shown. Again, four major clusters are formed:

– *K1*: *1, 23, 11, 42, 33, 34, 5, 12, 6, 9, 31, 19, 20, 14, 37, 10, 28, 29, 36, 39*;
– *K2*: *2, 27, 22, 40, 38, 13, 16, 21, 15, 18, 41, 45*;
– *K3*: *3, 4, 7, 30, 12, 26, 24, 25*;
– *K4*: *8, 32, 43, 35, 44.*

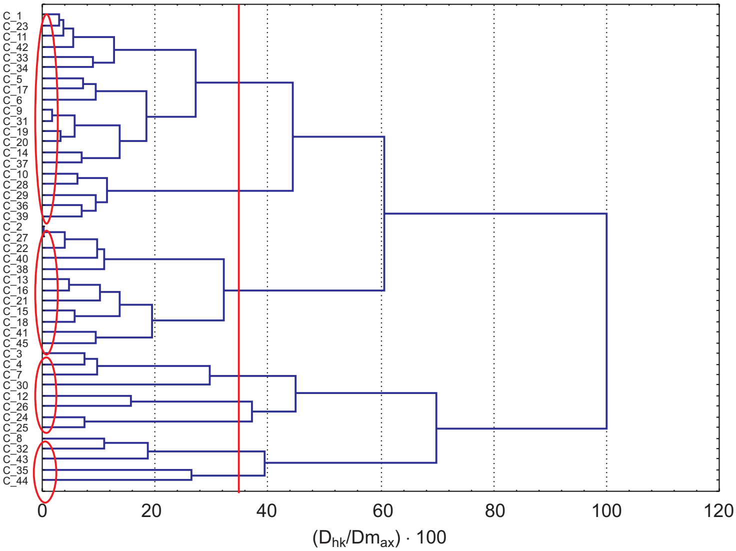

Fig. 4. Hierarchical dendrogram for 45 patients with 15 medical parameters

It is important to determine the structure of the patient data set with respect to the discriminating clinical parameters for each one of the clusters formed. It will help to understand better some specific features of the prolactinoma patients by their clinical indicators after process of treatment. The elimination of outliers is quite important in this situation as the estimation of the discriminators is based on calculation of the average value of each parameter for each cluster.

In Table 3 the average values for the clinical parameters for each cluster are given.

For some of the clinical indicators the averages are statistically equal: BMI, HGB, RBC, PLT, ALB, GLU, TRIGLI, and CORT. It means that the whole group of patients does not show any sensitivity to the identified metabolic syndrome factor (BMI, GLU, TRIGLI), to the blood oxidation factor (HGB, RBC) and to blood damaging factor (PLT, ALB, CORT). Thus, they cannot serve as discriminators for the patterns of patients.

The rest of the clinical indicators could play a discriminating function. The patients belonging to *K1* do not show any specific response of discriminating indicators. They

Table 3

Average values for each clinical parameter in each cluster

Variable	K-1	K-2	K-3	K-4
BMI	23.7	**32.5**	32.3	28.5
ESR	9.9	5.8	***14.4***	14.0
HGB	134.7	**145.8**	129.5	117.8
RBC	4.4	**5.0**	4.3	4.0
PLT	**254.5**	227.5	204.1	252.8
ALB	39.3	**40.7**	31.0	34.9
GLU	4.6	5.0	**5.2**	4.0
CHOL	4.2	4.4	4.6	***6.5***
LDL	2.9	2.7	2.1	***4.9***
TRIGL	0.8	**1.5**	**1.5**	1.4
ALAT	13.6	***24.2***	12.4	21.2
CK	50.6	69.4	59.6	***70.0***
PROLAC	443.0	398.4	170.0	***571.0***
FSH	6.8	5.6	***36.9***	29.3
CORT	373.9	**382.4**	348.0	154.8

Patients with numbers 1 to 39 are female and 40 to 45 male patients.

have relatively low values of BMI, GLU, CHOL, LDL, acceptable level of PROLAC and could be concluded that they form a pattern of *"patients of good health status"*. This is the group with most members (20).

The cluster *K2* (12 members) is characterized by the specific (high) level of ALAT which is probably an indication for some problems with the liver function. This group forms a pattern of patients with highest levels of BMI, HGB, RBC, ALB, TRIGLI, CORT, which, although not discriminating parameters, indicate for a still pathological status. Thus, this pattern of patients could be named "*patients still needing care and testing*". Probably, this group is formed by patients with higher level of initial problems – overweight, worse blood indicators, *etc*.

The next small cluster (8 patients) *K3* is characterized by highest levels of ESR and FSH (also GLU to some extent) but low levels of CHOL and LDL, ALB and PROLAC. This is a specific pattern of "*patients with good general status but needing improving of the blood parameters*".

The last cluster *K4* (5 patients) includes the most of the male patients and could be described as pattern of "*male prolactinoma specificity*". It shows surprisingly high level of PROLAC (it has to be mentioned that the outlier patient 41 is a male patient).

Conclusions

Specific relationships were revealed between the clinical parameters determined for prolactinoma patients. The formation of several clusters of similarity offers the opportunity for optimization of the procedure for clinical control by reducing the number of indicators necessary for rapid testing. Further, various patterns of similarity between the patients included in the group of observation were found: patients with good health status, patients needing additional care and observation, patients needing specific care to improve the blood parameters and male patients (as a separate pattern). The extraction of the indicator clinical parameters for each pattern allows a better decision making with respect to the health status of prolactinoma patients.

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INTERPRETACJA STATYSTYCZNA WIELOWYMIAROWYCH DANYCH KLINICZNYCH PACJENTÓW Z PROLAKTYNEMIĄ

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Abstrakt: Przeprowadzone badania pacjentów z prolaktynemią wykazały istnienie pewnych zależności pomiędzy parametrami klinicznymi, umożliwiających optymalizację procedur monitorowania stanu zdrowia za pomocą mniejszej liczby wskaźników. Taką optymalizację można osiągnąć dzięki interpretacji wartości parametrów za pomocą wielowymiarowych metod statystycznych, za pomocą których wykazano istnienie skorelowanych grup zmiennych wskaźnikowych. Dodatkowo stwierdzono istnienie czterech grup pacjentów z prolaktynemią, charakteryzujących się specyficznymi wskaźnikami klinicznymi. Informacje te mogą być wykorzystane do lepszej oceny stanu zdrowia pacjentów.

Słowa kluczowe: prolaktynemia, dane kliniczne, obróbka danych, analiza skupień, analiza głównych składowych

Varia

INVITATION FOR ECOpole ’13 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 22nd annual Central European Conference ECOpole ’13, which will be held in 23–26.08.2013 (Wednesday–Saturday) in Hotel Ziemowit in Jarnoltowek, PL.

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

- **SI Chemical Pollution of Natural Environment and Its Monitoring**
- **SII Environment Friendly Production and Use of Energy**
- **SIII Forum of Young Scientists and Environmental Education in Chemistry**
- **SIV 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 (5–8 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.

The deadline for sending the Abstracts is **15th July 2013** and for the Extended Abstracts: **1st October 2013**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2013**) on the Conference website:

ecopole.uni.opole.pl

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

The Conference fee is 400 € (covering hotel, meals and transportation during the Conference). It could be reduced (to 250 €) for young people actively participating in the Forum of Young Scientists. But the colleague has to deliver earlier the Extended Abstract (5–8 pages) of his/her contribution (deadline is on **15.08.2013**), and a recommendation of his/her Professor.

Fees transferred after **1st September 2013** are 10% higher.

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 '13 website).

After the ECOpole '13 Conference it will be possible to publish electronic version of presented contributions (oral presentations as well as posters) on the website.

Further information is available from:
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Conference series

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20. 2011 CEC ECOpole '11 Zakopane
21. 2012 CEC ECOpole '12 Zakopane

ZAPRASZAMY DO UDZIAŁU
W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI

SUBSTANCJE CHEMICZNE
W ŚRODOWISKU PRZYRODNICZYM
w dniach 23-26 X 2013, w Hotelu Ziemowit w Jarnółtówku

Będzie to **dwudziesta druga z rzędu** konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole ’13 będą zgrupowane w czterech Sekcjach:

- **Chemiczne substancje w środowisku przyrodniczym oraz ich monitoring**
- **SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie**
- **SIII Forum Młodych (FM) i Edukacja prośrodowiskowa**
- **SIV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi**

Materiały konferencyjne będą opublikowane w postaci:

- abstraktów (0,5 strony formatu A4) na CD-ROM-ie,
- rozszerzonych streszczeń o objętości 5–8 stron w półroczniku *Proceedings of ECOpole,*
- artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (*Ecol. Chem. Eng.*) ser. A i S oraz w półroczniku *Chemistry – Didactics – Ecology – Metrology* (*Chemia – Dydaktyka – Ekologia – Metrologia*).

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5–1,0 strony (wersja cyfrowa) planowanych wystąpień upływa w dniu 15 lipca 2013 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 31 lipca 2013 r. na stronie webowej konferencji:

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Aby praca (dotyczy to także streszczenia, które powinno mieć tytuł w języku polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami stawianymi artykułom drukowanym w czasopismach Ecological Chemistry and Engineering ser. A oraz S, które są dostępne w wielu bibliotekach naukowych w Polsce i za granicą. Zalecenia te są również umieszczone na stronie webowej Towarzystwa Chemii i Inżynierii Ekologicznej:

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Po konferencji zostaną wydane 5–8-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te winny być przesłane do **1 października 2013 r.** Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej.

Koszt uczestnictwa w całej konferencji wynosi 1600 zł (w tym 23% VAT) i pokrywa opłatę za udział, koszt noclegów i wyżywienia oraz materiałów konferencyjnych. Jest możliwość udziału tylko w jednym wybranym przez siebie dniu, wówczas opłata wyniesie 1100 zł i będzie upoważniała do uzyskania wszystkich materiałów konferencyjnych, jednego noclegu i trzech posiłków (śniadanie, obiad, kolacja).

Opłata dla magistrantów i doktorantów oraz młodych doktorów biorących aktywny udział w Forum Młodych może być zmniejszona do 1000 zł (w tym 23% VAT) przy zachowaniu takich samych świadczeń. Osoby te winny dodatkowo dostarczyć: rozszerzone streszczenia (5–8 stron) swoich wystąpień (**do 15.08.2013 r**.). Jest także wymagana opinia opiekuna naukowego.

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Wszystkie wpłaty powinny być dokonane na konto Towarzystwa Chemii i Inżynierii Ekologicznej w Banku Śląskim:

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i mieć dopisek ECOpole ’13 oraz nazwisko uczestnika konferencji

Streszczenia oraz program konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także zamieszczony na stronie webowej konferencji

Po konferencji będzie możliwość opublikowania elektronicznej wersji prezentowanego wystąpienia (wykładu, a także posteru) na tej stronie.

Prof. dr hab. inż. Maria Wacławek
Przewodnicząca Komitetu Organizacyjnego
Konferencji ECOpole ’13

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[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.

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[7] Simeonov D, Spasov L, Simeonova P. Statistical calibration of model solution of analytes. Ecol Chem Eng A. Forthcoming 2012.

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Druk: „Drukarnia Smolarski", Józef Smolarski, 45–326 Opole, ul. Sandomierska 1. Objętość: ark. wyd. 13,50, ark. druk. 11,00. Nakład: 350 egz. + 5 nadb. aut.