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SPIS TREŚCI

VARIA

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EFFECT OF UREA AND UREA WITH UREASE INHIBITOR ON YIELDS AND NITROGEN AND CADMIUM CONTENT IN POTATOES

WPŁYW MOCZNIKA I MOCZNIKA Z INHIBITOREM UREAZY NA PLONOWANIE ORAZ ZAWARTOŚĆ AZOTU I KADMU W ZIEMNIAKACH

Abstract: Worldwide the urea fertilisers are the fastest growing and most commonly used source of nitrogen in agriculture. The benefits of using urea as a fertiliser are due to its high nitrogen content (approximately 46 % nitrogen), non polarity, high solubility, and low costs for manufacture, storage, and transport. Among the various available mitigation tools, urease inhibitors like NBPT (N-(n-butyl) thiophosphoric triamide) have the highest potential to improve the efficiency of urea by reducing N losses, mainly via ammonia volatilization. In 2011 and 2012 a small-plot experiment was established with the potato 'Karin' variety. The experimental locality was Zabcice, ca 30 km south of Brno, a maize-growing region. Prior to planting both mineral fertilisers (urea and urea with urease inhibitor NBPT – UREA stabil) were applied to the soil surface. During planting these fertilisers were incorporated into the soil. The experiment involved 7 treatments: 54, 72, 90 kgN $\cdot$ ha^{-1} as urea, 54, 72, 90 kgN $\cdot$ ha^{-1} as UREA stabil and unfertilised control. Each treatment was repeated 4 times. The focus of the experiment was to monitor the effect of two different fertilisers and different N-doses on the yields of potato tubers and content of nitrogen (N) and cadmium (Cd) in tubers and tops (stems + leaves).

In 2011 the contents of nitrogen in the tubers fluctuated between 14.3 and 15.6 g $\cdot$ kg^{-1} d.m. and in the tops between 29.7 and 40.9 g $\cdot$ kg^{-1} d.m. The contents of cadmium in tubers ranged between 0.14 and 0.17 mg $\cdot$ kg^{-1} d.m. and in tops between 0.50 and 0.72 mg $\cdot$ kg^{-1} d.m. In 2011 the tuber yields fluctuated

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irregularly, i.e. between 17.0 and 32.9 Mg · ha^{-1}. In 2012 the nitrogen contents in tubers ranged between 16.0 and 17.3 g · kg^{-1} d.m. and in the tops between 23.9 and 36.9 g · kg^{-1} d.m. Cadmium contents in tubers fluctuated between 0.13 and 0.20 mg · kg^{-1} d.m. and in the tops between 0.35 and 0.64 mg · kg^{-1} d.m. In 2012 the tuber yields fluctuated irregularly between 25.2 and 33.9 Mg · ha^{-1}.

Based on the results we can conclude that both fertilisers (urea, UREA stabil) were reflected in the N and Cd contents of the biomass of potatoes irregularly in dependence on the year, rate of fertiliser and analysed plant organ (tubers, tops). In both years the contents of N and Cd were higher in the tops. Tuber yields fluctuated irregularly in dependence on the year and rates of nitrogenous fertilisers.

Keywords: urea, urease inhibitor, tubers, tops, cadmium, nitrogen, yield

Introduction

Urea is a widely used N fertiliser in agriculture worldwide [1]. In soil, urea is hydrolyzed by urease to NH_3 and CO_2 with a rise in pH and an accumulation of NH_4^+ [2]. About 5–30 % of the urea N is lost as volatilised NH_3. Implementation of NH_3 mitigation strategies is crucial in order to reduce both the economic and environmental impact associated with NH_3 losses from urea application [3]. High concentrations of NH_3 in the atmosphere can result in formation of the greenhouse gas N_2O and acidification of soil and surface waters [4].

One of the most promising ways to improve the efficiency of urea is to use urease inhibitor. This slows the conversion of urea to NH_3, and hence reduces the concentration of NH_4^+ present in the soil solution and the potential for NH_3 volatilisation and seedling damage. Slowing the hydrolysis of urea allows more time for the urea to diffuse away from the application site or for rain or irrigation to dilute urea and NH_4^+ concentration at the soil surface and increase its dispersion in the soil [5]. One of the most frequently used inhibitors is NBPT (N-(n-butyl) thiophosphoric triamide) which reduces the rate of urea hydrolysis and ammonia losses in various soils [6]. Its only disadvantage is that its effect is time-limited and usually lasts one to two weeks [7].

Nitrogen fertilisation has a considerable effect on yields and quality of tubers, especially on the content of starch and protein. Proteins (amino acids) are compounds of potato tubers of very high quality which have a favourable effect on the human organism. Nevertheless excessive amounts of nitrogen may reduce yields [8].

Cadmium is a heavy metal and as such it is not desirable in plant products. In higher amounts Cd may jeopardise the health of humans and animals [9]. According to McLaughlin et al [10] and Oborn et al [11] the accumulation of Cd may reach dangerous levels on low-acid soils, with a low content of organic substances and high content of Cd. The Decree 13/1994 Coll. on the maximal admissible amount of heavy metals in the soils, in force in the Czech Republic [12], gives 0.4 mgCd · kg^{-1} as the maximal amount for light soils and for other soils less than 1.0 mgCd · kg^{-1}. Soils in the Czech Republic contain on average 0.13–0.52 mgCd · kg^{-1}. The heaviest contamination of plants occurs in cases when the plants take up Cd from the soil [13]. The soil pH also greatly affects the solubility and accessibility of Cd; when the pH value decreases most of the ions increase their mobility [14]. Cd is accumulated most of all in roots, next in vegetative organs and the least in generative organs [15]. Jönsson and Asp [16] reported that increasing rates of nitrogen reduced the Cd content in potato tubers.

The objective of the two-year experiments was to compare nitrogen fertilisation with urea and urea with the urease inhibitor on yields and contents of nitrogen and cadmium in tubers and tops of potatoes, 'Karin' variety.

Material and methods

The small-plot experiment was established at the School Farm in Zabcice near Brno (altitude 179 m) in 2011 and 2012. The locality lies in a warm maize-growing region and the soil type is gley fluvisol. The agrochemical properties of the medium heavy soil characterised as fluvisol were evaluated prior to establishment of the trial (Table 1).

Table 1

Agrochemical characteristics of the soil (Mehlich III)

Property	pH/$CaCl_2$	P	K	Ca	Mg
		$[mg \cdot kg^{-1}]$			
Value Estimation	5.9 weak acid	79 suitable	197 good	3.133 good	346 very high

The soil was leached with the Mehlich III (CH_3COOH, NH_4F, HNO_3, NH_4NO_3, EDTA) agent. K, Ca and Mg were assessed using AAS (Atomic Absorption Spectrometry), P was assessed using colorimetry.

For the experiment we used the early potato, 'Karin' variety, which was planted out on 7 April 2011 and 29 March 2012, spacing 750 × 250 mm. The variety is an excellent table variety. Prior to planting out the fertilisers (urea and urea with urease inhibitor NBPT-UREA stabil) were applied onto the soil surface and during planting were incorporated into the soil. The experiment consisted of 7 treatments (Table 2). Each treatment was repeated 4 times.

Table 2

Pattern of experiment

Variant	Fertilisation	N rate $[kg \cdot ha^{-1}]$
1	unfertilized control	—
2	urea	54
3	urea	72
4	urea	90
5	UREA stabil*	54
6	UREA stabil	72
7	UREA stabil	90

* Urea with urease inhibitor NBPT.

During vegetation the stands were treated with chemical preparations for weed, disease and pest control. The stands were harvested on 12 July 2011 and 14 August 2012 and samples were taken for assessments of tubers yields, and nitrogen and cadmium contents in the potato tubers and tops. The samples were dried, homogenised and wet-mineralised ($H_2SO_4 + H_2O_2$ to assess N according to the method of Kjeldahl; $HNO_3 + H_2O_2$ to assess Cd using AAS – Atomic Absorption Spectrometry). The results were processed statistically by variance analysis and then tested according to Scheffe ($p < 0.05$).

Results and discussion

Tuber yields were higher in 2012 than in 2011 (Table 3 and 4) and one of the reasons could be that the amount of rainfall during vegetation was higher.

Table 3

Tuber yields and content of N and Cd in potato tubers and tops in 2011

Variant No.	Pattern	N rate	Yields	N $[g \cdot kg^{-1}$ d.m.]		Cd $[mg \cdot kg^{-1}$ d.m.]	
		$[kg \cdot ha^{-1}]$	$[Mg \cdot ha^{-1}]$	tubers	tops	tubers	tops
1	unfertilized control	—	17.7 c	14.3 a	40.8 a	0.17 a	0.62 a
2	urea	54	17.0 c	14.7 a	37.7 b	0.15 a	0.66 a
3	urea	72	24.4 b	15.2 a	40.9 a	0.16 a	0.56 a
4	urea	90	32.9 a	14.5 a	32.6 c	0.16 a	0.50 a
5	UREA stabil*	54	23.4 b	14.5 a	36.4 b	0.15 a	0.72 a
6	UREA stabil	72	17.2 c	15.3 a	36.0 b	0.14 a	0.66 a
7	UREA stabil	90	18.5 c	15.6 a	29.7 c	0.16 a	0.62 a

* Urea with urease inhibitor NBPT; different letters (a, b, c) indicate significant differences between treatments.

Table 4

Tuber yields and content of N and Cd in potato tubers and tops in 2012

Variant No.	Pattern	N rate	Yields	N $[g \cdot kg^{-1}$ d.m.]		Cd $[mg \cdot kg^{-1}$ d.m.]	
		$[kg \cdot ha^{-1}]$	$[Mg \cdot ha^{-1}]$	tubers	tops	tubers	tops
1	unfertilized control	—	33.9 a	16.0 a	26.1 c	0.14 b	0.57 ab
2	urea	54	30.5 ab	16.4 a	30.6 b	0.17 ab	0.35 d
3	urea	72	25.2 c	16.7 a	36.9 a	0.15 ab	0.46 c
4	urea	90	28.6 b	17.2 a	30.3 b	0.20 a	0.53 b
5	UREA stabil*	54	30.4 ab	16.0 a	23.9 c	0.13 b	0.64 a
6	UREA stabil	72	30.0 ab	17.2 a	27.1 bc	0.15 ab	0.47 c
7	UREA stabil	90	25.7 c	17.3 a	33.9 ab	0.15 ab	0.50 bc

* Urea with urease inhibitor NBPT; different letters (a, b, c) indicate significant differences between treatments.

In 2011 the lowest dose of N using urea as the fertiliser to a non significant degree lowered tuber yield (by 4 %). Medium and the biggest rates of N significantly affected yields of tuber causing an increase by 38 % and 86 %, respectively, in relation to the control treatment. An opposite effect was observed in case of N in form of urea applied with urease inhibitor (UREA stabil) as the fertiliser. The lowest dose of N significantly increased tuber yield (by 32 %) but medium and the biggest ones had non significant effect on potato yielding. Medium dose in small extent lowered (by 3 %) and the biggest one it small degree increased tuber yield (by 5 %) in relation to the control treatment.

By contrast in 2012 the highest tuber yield was noted in control treatment. The smallest N doses did not significantly affect potato yielding, lowering tuber yield by 10 % in both fertiliser variants in comparison with control. The medium and biggest doses of urea dropped significantly tuber production by 26 % and 16 %, respectively. After application of medium and the biggest N doses using UREA stabil decrease of tuber yield was observed (by 12 % and 24 %, respectively) but only in case of biggest dose it triggered of significant reaction in amount of tuber yield. It could be caused by rainfall during the first days after planting the potatoes which might have flooded out some of the fertilisers from the soil.

Coelho et al [17] and Gileto et al [18] discovered that tuber yields increased with increasing rates of N fertilisers. This was confirmed by Poljak et al [19]. In their experiments tuber yields increased (34.38; 38.70; 38.92; 39.48 and 39.71 $\mathrm{Mg \cdot ha^{-1}}$) along with rates of N (0; 100; 150; 200 and 250 $\mathrm{kg \cdot ha^{-1}}$) and the N content in tubers enhanced as well (16.2; 17.0; 17.1; 16.4 and 17.9 $\mathrm{g \cdot kg^{-1}}$). Jurkowska et al [20] who studied an effect of dicyandiamide and thiourea as inhibitors slowing N transformation in soil, observed significant improve of biomass yield of different plant species.

No significant differences between the two years were seen among the treatments in the N contents in tubers (Table 3 and 4). Braun et al [21] explored the effect of nitrogen fertilisers on the content of N in potato tubers. Likewise they discovered that rates of 0; 50; 100; 200 and 300 $\mathrm{kgN \cdot ha^{-1}}$ had no effect on the N content in tubers.

The N content in potato tops was higher than in tubers, from 1.90 to 2.85 times in 2011 and from 1.49 to 2.29 times in 2012, and was very variable with regard to the rate or type of fertiliser in both years. In 2011 the biggest N content was observed in tops of control treatment. Medium N dose applied as urea did not affect N content in tops in comparison with control, and the smallest and the biggest doses substantially lowered it by 8 % and 10 %, respectively. All doses of N applied as urea with urease inhibitor significantly decreased N content in tops, especially the biggest one, by 11 %, 12 % and 10 %, respectively.

In 2012 application of the smallest, medium and the biggest doses of N as urea substantially increased N content in tops, by 17 %, 41 % and 16 %, respectively. The smallest and medium doses of N applied as UREA stabil did not affect significantly N content in tops in relation to control treatment. The highest dose of N applied in this form substantially affected N content in potato tops causing its increase by 30 %, and it was the highest N content in tops in 2012.

Poljak et al [19] in their experiments stated enhanced N content in tubers (16.2; 17.0; 17.1; 16.4 and 17.9 g · kg^{-1}) as a reaction on increased doses of N application (0; 100; 150; 200 and 250 kg · ha^{-1}). Jurkowska et al [20] observed different reactions of plants on N inhibitors application. Increase of N content in plants was an effect of dicyandiamide application, and opposite plant response was noted after thiourea use.

The Cd content in tubers ranged from 0.14 to 0.17 mg · kg^{-1} in 2011 and from 0.13 to 0.20 mg · kg^{-1} in 2012. Differences in Cd contents in the tubers between the years and among the treatments were minimal. In both years the Cd content in tops was higher than in tubers, from 3.13 to 4.80 times in 2011 and from 2.06 to 4.92 times in 2012. The year-on-year content of Cd in tops was balanced but significant differences were discovered among the treatments. However, these differences were very irregular and that it why it is difficult to reach unambiguous conclusions in terms of the type or rate of the fertiliser.

In 2011 the highest Cd accumulation was stated in tubers of control plants. Both N fertilizers application decrease Cd content in potato tubers by 6–16 %. Urea and urea with urease inhibitor application changed differently Cd content in tops. The lowest N dose applied as urea caused increase (by 6 %) but medium and the highest decreased Cd content (by 10 % and 19 %, respectively). Equivalent N doses in UREA stabil increased by 16 % and 6 % or did not change Cd content in tops, respectively. These changes were not substantial.

In 2012 all N doses applied as urea increased Cd content in potato tubers (by 21 %, 7 % and 43 %, respectively) but only the highest N dose caused substantial change. N applied in UREA stabil did not affect significantly Cd content in tubers. Increasing N doses in urea decreased Cd content in potato tops (by 39 %, 19 % and 7 %, respectively) and two smaller N doses caused substantial change. The smallest N dose applied in urea with urease inhibitor increased Cd content in tops (by 12 %), and two higher N doses decreased content of this metal (by 18 % and 12 %, respectively) but only medium dose had significant effect.

Larsson and Asp [22] reported that the Cd content in potato tubers decreased with increasing rates of nitrogen fertiliser. Hlusek et al [23] maintain an opposite opinion; the Cd content in potato tubers increased along with N rates from 60 to 120 kgN · ha^{-1}. A similar situation was monitored in the second year of the experiment after the application of urea (Table 4) when the highest concentration of Cd in the potato tubers was achieved with the highest rate of nitrogen (90 kgN · ha^{-1}). The changes in Cd content in potato organs in both years of investigation may be a result of differences in amount of precipitation during the vegetation season. Wisniowska-Kielian [24] in her studies on the effect of soil moistness on heavy metals absorption by different plants stated substantial changeability in Cd content in plant dependent on species and plant organ.

Conclusions

1. Potato tuber yields were higher in 2012 than in 2011 and one of the reasons could be bigger sum of rainfall during the vegetation season.

2. In both years the tuber yields fluctuated irregularly and the dependence on type or rate of fertiliser was different. In 2011 two bigger N rates applied in urea and the lowest dose in UREA stabil significantly increased yield of tubers, in relation to the control treatment. In 2012 two bigger N rates in urea and the biggest N doses in UREA stabil significantly reduced tuber yield.
3. The N content in potato tubers was lower from 1.49 to 2.85 times than in tops, and its content in tubers changed insignificantly in all treatments of both years.
4. N content in tops in 2011 significantly decreased after the smallest and the biggest N doses in urea and all N doses in UREA stabil, in comparison with control treatment. In 2012 application of urea and the highest N dose in UREA stabil substantially increased N content in tops.
5. The Cd content in tubers was lower from 2.06 to 4.92 times than in tops, and only in 2012 the highest N dose applied in urea significantly increased Cd content in tubers, in relation to the control treatment.
6. Substantial decrease in Cd content in potato tops was noted only in 2012 when two smaller N doses in urea and medium N dose in UREA stabil were applied.
7. Considering the effect of the weather of the year deems that it is necessary to repeat the experiments.

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WPŁYW MOCZNIKA I MOCZNIKA Z INHIBITOREM UREAZY NA PLONOWANIE ORAZ ZAWARTOŚĆ AZOTU I KADMU W ZIEMNIAKACH

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Abstrakt: Na całym świecie nawozy mocznikowe są najbardziej dynamicznie rozwijającym się i najczęściej stosowanym źródłem azotu w rolnictwie. Korzyści ze stosowania mocznika jako nawozu wynikają z dużej zawartości azotu (około 46% azotu), jego niepolarności, dobrej rozpuszczalności oraz niskich kosztów produkcji, przechowywania i transportu. Wśród różnych dostępnych narzędzi ograniczania dostępności azotu, inhibitory ureazy, takie jak NBPT (N-(n-butylo) triamid tiofosforowy) mają największy potencjał do poprawy efektywności mocznika poprzez zmniejszenie strat N, głównie przez ulatnianie amoniaku. W latach 2011 i 2012 założono małopoletkowe doświadczenie z ziemniakami odmiany ‘Karin’, zlokalizowane w miejscowości Žabčice, około 30 km na południe od Brna, w regionie uprawy kukurydzy. Przed sadzeniem zastosowano obydwa warianty nawożenia mineralnego (mocznik i mocznik z inhibitorem ureazy NBPT-UREA stabil) na powierzchnię gleby. W czasie sadzenie nawozy zostały wymieszane z glebą. Doświadczenie obejmowało 7 obiektów: 54, 72, 90 kgN $\cdot$ ha^{-1} jako mocznik, 54, 72, 90 kgN $\cdot$ ha^{-1} jako UREA stabil oraz nienawożony obiekt kontrolny, każdy w 4 powtórzeniach. Celem doświadczenia było zbadanie działanie dwóch różnych nawozów i różnych dawek N na wielkość plonu bulw ziemniaka oraz zawartość azotu (N) i kadmu (Cd) w bulwach i łętach (łodygi + liście).

W 2011 r. zawartość azotu w bulwach wahała się od 14,3 do 15,6 g $\cdot$ kg^{-1}, a w łętach od 29,7 do 40,9 g $\cdot$ kg^{-1} s.m. Zawartość kadmu w bulwach wahała się od 0,14 do 0,17 mg $\cdot$ kg^{-1}, a w łętach od 0,50 do 0,72 mg $\cdot$ kg^{-1} s.m. W 2011 r. plony bulw zmieniały się nieregularnie, tj. od 17,0 do 32,9 t $\cdot$ ha^{-1}. W 2012 r. zawartość azotu w bulwach wahała się od 16,0 do 17,3 g $\cdot$ kg^{-1}, a w łętach od 23,9 do 36,9 g $\cdot$ kg^{-1} s.m. Zawartość kadmu w bulwach wahała się od 0,13 do 0,20 mg $\cdot$ kg^{-1}, a w łętach od 0,35 do 0,64 mg $\cdot$ kg^{-1} s.m. W 2012 r. plony bulw zmieniały się nieregularnie, od 25,2 do 33,9 Mg $\cdot$ ha^{-1}.

Na podstawie uzyskanych wyników można stwierdzić, że obydwa warianty nawożenia (mocznik, UREA stabil) powodowały nieregularne zmiany zawartości N i Cd w biomasie ziemniaka w zależności od roku, dawki azotu i analizowanego organu rośliny (bulwy, łęty). W obydwu latach łęty zawierały więcej N i Cd niż bulwy. Plony bulw zmieniały się nieregularnie w zależności od roku i dawki nawozów azotowych.

Słowa kluczowe: mocznik, inhibitor ureazy, bulwy, łęty, kadm, azot, plony

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FERTILIZERS APPLIED IN MODERN AGRICULTURE ARE NEITHER HARMFUL NOR TOXIC

NAWOZY STOSOWANE W NOWOCZESNYM ROLNICTWIE NIE SĄ ANI SZKODLIWE, ANI TOKSYCZNE

Abstract: The paper presents definition of a modern agriculture as a man activity in very broad natural and social interactions. The paper also presents critical views on modern farming and fertilization, as well as indicates that the proper use of artificial fertilizers is and should be an important factor of crop productivity. The paper gives the list of the most basic chemical fertilizers and current level of fertilizing components use in Poland. The title of the paper, which is also the main thesis of the study, fully confirms the legitimacy of a view that chemical fertilizers are neither harmful nor toxic, and it is in the opposition to the common and false opinions that present chemical fertilizers as dangerous for humans, which is of course completely groundless.

Keywords: agriculture definition, chemical fertilizers, fertilization criticism

Definitions of agriculture

Agriculture is such a large and important area of human civilization, that a concise definition of the forms and scope of activity seems to be extremely difficult. Perhaps the first and unbeatable definition of agriculture is attributed to the Roman speaker Cicero: “Agriculturae proxima sapientiae est”. This is very accurate and interestingly still true definition. As it seems, the best modern definition of agriculture, that can be considered as quite close to perfection, as it is accurate and concise and actually fully correct, is “Agriculture is an activity of man primarily aimed at the production of food, fiber and other materials (as well as power and fuel) by the controlled use of (mainly terrestrial) plants and animals.” by [1].

Generally, to formulate any definition in science is not an easy task, because it turns out that it is difficult to write a good scientific definition, which would not include any exceptions. Therefore, an attempt to develop a schematic, *ie* glossary, definition of modern agriculture, which is definition based on a set of terms including: firstly, the

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main particular agricultural terms, secondly, two main groups of concepts forming the complete definition of agriculture, and thirdly, indicating the share of these two groups of contained concepts as the definition of modern agriculture. Thus, it can be assumed that the overall definition of agriculture in a schematic can distinguish one group (soil, water, air, plant, fertilizer, energy, time) estimated for 10 % of its importance in agriculture, and the second group (human, knowledge, information) estimated for 90 % of importance in modern agriculture.

Modern agriculture

Modern agriculture uses a wide spectrum of different terms, that are sometimes inappropriate or incorrectly defined; the simplest example to specify is *eg* "conventional" as opposed to 'organic' farming. For further discussion, it would be necessary to add three assumptions: first, that the main product of agriculture is the primary yield, which is useful parts of plants, second, that agriculture produces only the raw agricultural materials, and third, that food is produced by the food industry, and of course there are also exceptions, for there are also products of direct consumption in agriculture, but when such products are sold, must be subject to the market rules, *ie* must keep some standards as any commodity to trade.

If common nomenclature to accept, distinguishing such terms as 'conventional' and 'organic' farming is certainly not appropriate in the sense of the notions: 'conventional' and 'organic', and if it would be accepted as a correct statement, then very accurate comparison of the major differences between 'conventional farming' and 'organic farming' was presented by what is very well illustrated on a diagram. The graph shows that the distinction between these terms is significant, however it is not an issue associated with the use of fertilizers, but pesticides, and it is truth, indeed because chemical pesticides are very dangerous for man (Fig. 1) after [2].

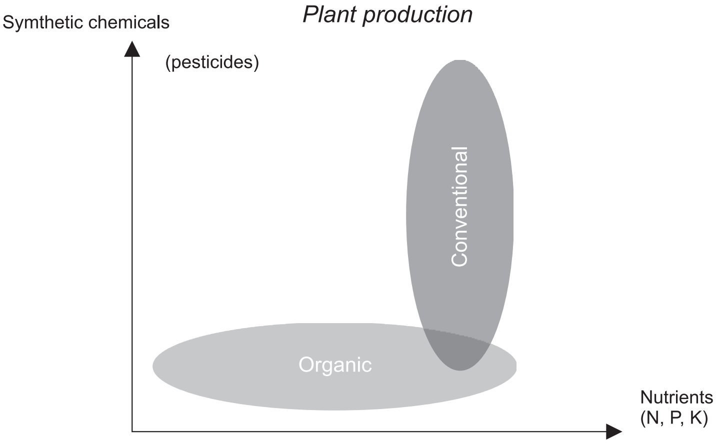

Fig. 1. Relationship between nutrient inputs and the use of synthetic compounds in organic and conventional plant production [2]

In the science, particularly in the applied sciences, and most particularly in agriculture, it had been that different soil tillage were initially made for centuries of human history, and later the theories proving the agricultural practices were developed. Theories to practical applications using modern methods of different treatments and cultivations, are proposed for now and for the future [3–5] presented a wonderful publication containing considerations of what can result from “organic farming”, with a title being some kind of a reminder and warning. Meanwhile, some views about the dangers of chemical fertilizers are still supported by suggestions that artificial fertilizers used in agriculture are agents that contaminate soils and the environment [6].

Current definitions of ‘conventional farming’ and ‘organic farming’, whatever they mean, are methods recommended in ‘organic farming’, are usually amended without any scientific evidence. Meanwhile, there is no scientific evidence for the superiority of ‘organic farming’ over ‘conventional farming’. Besides, the terminology itself is not correct, because ‘conventional’ means simply ‘traditional’, whereas the opposition to conventional is not newer, but older and organic manner of production, which is about 100 years earlier than conventional one. And perhaps it would be much more appropriate to refer to ‘conventional farming” as ‘modern farming’ and ‘organic farming’ as simply ‘medieval farming’. In addition, legal acts are also created that are to give an impression that ‘organic farming’ cares about human health. And it is commonly known that from a scientific point of view, there is no question about whether a phenomenon, view, or a method is consistent with the law, but about whether the phenomenon, view, or method is true or not.

Fertilization criticism

Based on many years of observation and research, simple and clear, and above all practically useful yet important, principles of fertilizer recommendations have been formulated indicating that high yields and the highest quality of crops can be achieved by different management ways and chemical methods of soil and plant analysis are only little precise and generalized assessment of a cropland. At the same time, the use of manure and fertilizers, taking into account the abundance of arable field and natural environment conditions are important for a good utilization of fertilizing components and reduction of environmental hazard. However, yields are often limited by climate, such as rainfall and temperature, or inappropriate physical and biological soil conditions, or increased susceptibility to plant diseases. A most interesting issue was to draw attention to the practically most important principle that before any fertilizer recommendation, a farmer should always consider which factor may actually limit the yield, because this way the disappointments can be avoided [7].

The history of fertilization taking into account the experimental fertilization schemes was concisely and interestingly described in the introduction to the considerations upon the main problem, which was to search for optimal fertilizing components ratios in a total summering rate of N, P, and K. However, it seems that in this work the most interesting was that applied mass of fertilizing nutrients are not important for plants, but amount of fertilizing nutrients affecting or taken up by crops, i.e. amount of fertilizing components expressed by amount of substance [8].

A new approach to fertilizer recommendations based on the use of the elemental composition in the entire above-ground parts of plants during the flowering stage to determine the fertilizing components ratios useful for practical fertilization, was also considered. This concept assumed that fertilization using lower rate of five fertilizing components (N, P, K, Mg, and S) and their appropriate ratios (N/P, N/K, N/Mg, and N/S) should lead to better results on the yielding than higher rates of only one or two, or even only three fertilizing components. In this fertilization, which component is the yield limiting factor should be also determined, and if the limiting fertilizing component would be, e.g. N, then the following ratios should be taken into consideration P/N, K/N, Mg/N, and S/N [9].

In theory and practice of fertilization, it was indicated that applied the initial and lower fertilizing component rate gives the greatest increased of the yield, whereas the effectiveness of higher fertilizing component rates always getting lower and lower and tending to zero. Thus, in modern crop productions, the fertilization should be on the sake of minimizing the use of fertilizing components, it means that only such fertilizing component rates should be use the only in the range of increase the yields, but never to tend to the optimizing of fertilization and maximizing of yields, and expect of the highest yields.

Chemical fertilizers in agriculture

There is large spectrum of available fertilizers for agricultural practice. It is very significant that the number of chemical compounds is the same for decades, so the assortment is formed from the same chemicals, obviously with new names, or different mixtures are produced from the same compounds, but then with variety names. In addition, producers of fertilizers do not unveil the constituent chemical compounds, and only content of fertilizing components are given. Then the problem is even worse, because the farmers often in their observations, and rarely scientists, reflect upon the influence of the fertilizer name on the yield size or crop quality.

Producers of fertilizers generally provide the content of main fertilizing component, and very rarely give the chemical compounds in fertilizers, and almost never give the elemental composition. What a pity, because natural materials recommend in the ‘organic farming’, in general in a form of crumbled or ground raw rock, may contain elements that should be not exist in fertilizers, and among these elements are sometimes unwanted radioactive elements; this is not mentioned, however, in the ‘organic farming’. Another example can be the application of manure or composted manure for ‘organic farming’, as wastes from a farm, which have no standards: neither chemical nor parasitological nor microbiological. Another example: as in the 19th century, today the phosphorus content in fertilizers is given in its oxide form. This also includes potassium and other nutrients and this cannot be changed neither by universities, nor by world fertilizer congresses, where the issue is recalled; it is the highest time to give the content of nutrients in their correct elemental forms. And the anachronism, is that phosphorus and potassium are not present in the oxide forms, neither in soils, nor in plants, nor in fertilizers.

No harmful chemical fertilizers

A background to the consideration is a compilation of basic chemical fertilizers including the four most important information about fertilizers: (1) name of fertilizer, (2) fertilizing compound, (3) content of the fertilizing component, (4) fertilizing nutrient. Distinction of these four characteristics is very useful in practice, because conscious farmer should know what forms of fertilizing nutrient will affect crops from the soil (Table 1).

Table 1

Common fertilizers and defined as approximate content of fertilizing components in Poland

Artificial and commercial fertilizers			
Fertilizer name	Fertilizing compound as chemical formula	Fertilizing component in %	Fertilizing nutrient as chemical form
Ammonium sulphate	$(NH_4)_2SO_4$	N 20 % S 24 %	NH_4^+ SO_4^{2-}
Sodium nitrate	$NaNO_3$	N 15 %	Na^+ NO_3^-
Potassium nitrate	KNO_3	N 13 % K 38 %	K^+ NO_3^-
Calcium nitrate	$Ca(NO_3)_2$	N 15 % Ca 15 %	Ca^{2+} NO_3^-
Ammonium nitrate	NH_4NO_3	N 34 %	NH_4^+ NO_3^-
Calcium ammonium nitrate	$NH_4NO_3 + CaCO_3$	N 28 %	NH_4^+ NO_3^-
Urea	$CO(NH_2)_2$	N 46 %	
Single superphosphate	$Ca(H_2PO_4)_2 + CaSO_4$	P 8 % S 12 %	Ca^{2+} $H_2PO_4^-$ SO_4^{2-}
Triple superphosphate	$Ca(H_2PO_4)_2$	P 20 %	Ca^{2+} $H_2PO_4^-$
Ground rock phosphate	$Ca_3(PO_4)_2$	P 13 %	Ca^{2+} $H_2PO_4^-$
Potassium chloride[1]	KCl	K 50 %	K^+ Cl^-
Potassium sulphate	K_2SO_4	K 41 % S 18 %	K^+ SO_4^{2-}
Magnesia kainite[2]	$KCl + K_2SO_4 + MgSO_4$	K 21% Mg 5 % S 10 %	K^+ Mg^{2+} SO_4^{2-} Cl^-
Kieserite	$MgSO_4$ H_2O	Mg 16 % S 22 %	Mg^{2+} SO_4^{2-}
Epsom salts	$MgSO_4$ $7H_2O$	Mg 10 % S 13 %	Mg^{2+} SO_4^{2-}
MAP[3] + DAP[4]	$NH_4H_2PO_4 + (NH_4)_2HPO_4$	N 18 % P 20 %	NH_4^+ $H_2PO_4^-$ HPO_4^{2-}
MAP[3] + DAP[4] + MOP[1]	$NH_4H_2PO_4 + (NH_4)_2HPO_4 + KCl$	N 18 % P 10 % K 20 %	NH_4^+ $H_2PO_4^-$ HPO_4^2 K^+

[1] MOP Muriate of potash; [2] Content of chemical components is very changing; [3] MAP Monoammonium phosphate; [4] DAP Diammonium phosphate.

Extensive studies upon the use of fertilizing component in Poland were carried out for a longer time with 5 years increment. However, it should be clearly stated that these results do not show a direct cause-effect relationship between use of fertilizing component and yields of these crops, because results are of global nature and nothing is known about it: where, when, and how these fertilizing components of fertilizers were applied. This study had been show in three parts: the first, use of fertilizing components and substances for soil de-acidification, the second as trends in the use of fertilizing components and alkali for soil de-acidification in subsequent periods. Calculated regression coefficients b_{yx} for the equation y = b + c in the adequate periods when was linear depending between of the features. And calculated values were marked with sign as (+) or (–), which is easy visible on graph (Fig. 2), and the third, yields was gives for the only four crops, because data of yields in the statistical source referring only to these crops yields were presented throughout the overall examined period. Finally, which was the most important in the presentation of this study that presented results can also easily indicate what were the yields without the use of chemical fertilizers, the good example of which was year 1946 (Table 2).

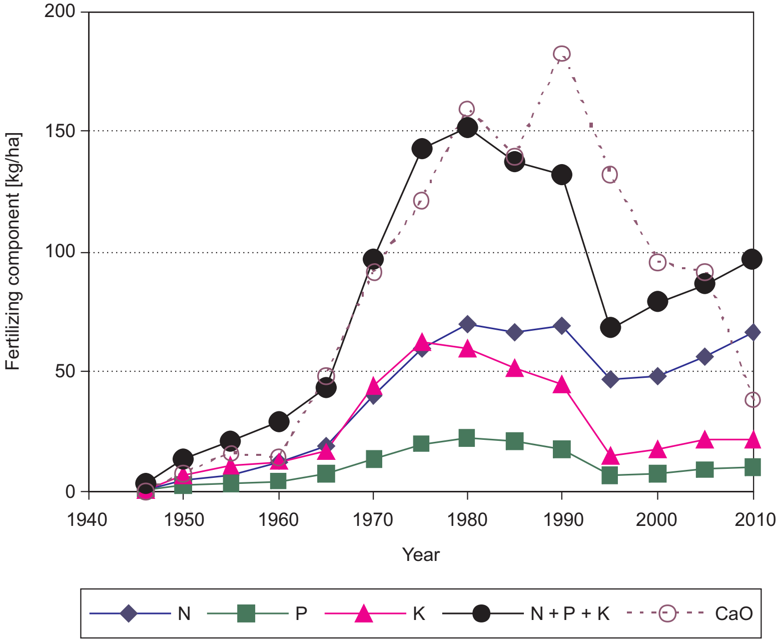

Fig. 2. Fertilizing components and liming use in Poland in the years 1946–2010

The evidence confirming the thesis in the paper title is a summary of the main compounds in chemical fertilizer (Table 1) along with chemical compounds that are widely use as food preservatives (Table 3). And the proof is easy and simple. The same chemical compounds that are chemical fertilizing compounds are also chemical food preservatives. Thus, the title of the work, which is also the main thesis of the study, fully confirms the validity of a view that chemical fertilizers are neither harmful nor toxic, which is opposite to the common and false opinions that chemical fertilizers as

Table 2

Fertilizing components use and crop yields estimated in the years 1946–2010 in Poland

Component	Year													
	1946	1950	1955	1960	1965	1970	1975	1980	1985	1990	1995	2000	2005	2010
	Fertilizing component N P K and CaO equivalent in kg/ha*													
N	1.1	4.6	6.7	12.3	19.4	40.2	60.1	69.6	66.1	68.9	46.6	48.4	56.3	66.3
P	0.8	2.2	3.1	3.9	7.1	13.3	20.3	22.4	20.6	17.8	6.8	7.3	8.9	9.9
K	1.2	6.7	10.6	12.7	16.5	44.0	62.4	59.7	51.3	45.1	14.6	17.2	21.3	21.2
N + P + K	3.1	13.5	20.4	28.9	43.0	97.5	142.8	151.7	138.0	131.8	68.0	79.2	86.5	97.4
CaO equiv.	0.4	7.1	15.9	14.1	48.3	90.9	120.8	159.7	139.4	182.4	131.9	95.1	91.5	38.1
Component	Component in kg/ha for respectively determined period with sign + as increase or sign – as decrease**													
N	+1.9										+1.3			
P	+0.7								–1.4			+0.3		
K	+0.8					+3.7		–1.2			+0.5			
N + P + K	+4.7								–7.0			+2.5		
CaO equiv.	+4.5										–5.7			
Crop	Yield in tons/ha*													
Wheat	0.88	1.28	1.49	1.69	2.60	2.32	2.83	2.60	3.43	3.96	3.60	3.23	3.95	4.39
Rye	0.90	1.28	1.41	1.54	1.84	1.56	2.25	2.16	2.47	2.61	2.56	1.88	2.41	2.68
Potato	11.2	13.8	10.0	13.2	15.4	18.4	18.0	11.3	17.4	19.8	16.4	19.4	17.6	21.1
Sugar beet	17.6	22.2	18.6	25.6	25.9	31.2	31.7	22.1	33.6	38.0	34.6	39.4	41.6	48.3

* The study based on Statistical Yearbook of the Republic of Poland, Central Statistic Office, Warszawa of 1946–2011; ** Calculated trend of increase or decrease fertilizing component use what easily see on Fig. 2.

Table 3

Chemical fertilizing compounds as well as chemical food preservatives

Chemical name	Chemical compound	Approximate element content						Food preservative
		N	P	K	Ca	Mg	S	
		[%]						
Ammonium sulphate	$(NH_4)_2SO_4$	21					24	E 517
Sodium nitrate	$NaNO_3$	16						E 251
Potassium nitrate	KNO_3	14		38				E 252
Calcium nitrate	$Ca(NO_3)_2\ 4H_2O$	12			17			
Ammonium nitrate	NH_4NO_3	35						
Urea	$CO(NH_2)_2$	46						E 927
Monocalcium phosphate	$Ca(H_2PO_4)_2\ H_2O$		24		16			E 341 (i)
Tricalcium phosphate	$Ca_3(PO_4)_2$		20		38			E 341 (iii)
Monoammonium phosphate	$NH_4H_2PO_4$	12	27					E 342
Diammonium phosphate	$(NH_4)_2HPO_4$	21	23					E 342
Potassium chloride	KCl			52				E 508
Potassium sulphate	K_2SO_4			45			18	E 515 (i)
Magnesium sulphate	$MgSO_4\ H_2O$					17	23	
Magnesium sulphate	$MgSO_4\ 7H_2O$					10	13	Medication
Deacidifying compound		[%]						
Calcium oxide	CaO				71			E 529
Calcium carbonate	$CaCO_3$				40			E 170 (i)
Magnesium oxide	MgO					60		E 530
Magnesium carbonate	$MgCO_3$					28		E 504 (i)
Acidifying compound		[%]						
Sulphur	S						100	
Calcium sulphate	$CaSO_4\ 2H_2O$				23		18	E 516

dangerous for humans, which is obviously completely groundless. A simple example of calculation that only shows the scale of the problem can be represented in following way. Let a chemical fertilizer was applied in the amount of 300 kg/ha to the field of 1 hectare. Assuming the area of 1 ha is 10000 m^2, tillage layer is 0.2 m deep, and soil bulk density is 1.5 Mg/m^3, then concentration this applied fertilizer in the soil would reach only concentration will be 0.01 %, and this is in soil, not in food. Although the ranges of different food preservative compounds are very broad, it can be assumed, with some stipulations, that the mean concentration of chemical food preservatives is about 0.01 %, and this is in food, not in soil.

Conclusions

The use of very high rate of fertilizing components applied in the crop fertilization, which based on the concept of nutrient requirements of crops and expected of forecast yields was the cause of the harmful effects applied of fertilizers in the field as well as in the natural environment.

However the fertilizer recommendations from the science point of view seemed to be proper and correct, nevertheless it led to the common views, that application of chemical compounds in agriculture began to be perceived as improper way in the present agriculture development.

In the modern agriculture can be use chemical fertilizers because fertilizing compound applied in the crop production are neither harmful nor toxic, however, the crop fertilization should be take into consideration the fertilizer recommendation as rational, reasonable, prudent, cautious, poise or balanced.

It is sure, that just chemistry is the science which has the biggest positive effect on development of agriculture *eg* discovery of nitrogen compounds synthesis, development of fertilizers production technology, development of soil and plant analysis, and many other discoveries, which gave the possibility of common use of chemical fertilizers and very significantly increased the crop productivity. Chemistry is in fact the boon of agriculture.

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NAWOZY STOSOWANE W NOWOCZESNYM ROLNICTWIE NIE SĄ ANI SZKODLIWE, ANI TOKSYCZNE

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Abstrakt: Praca przedstawia definicję nowoczesnego rolnictwa jako działalności człowieka w bardzo szerokich przyrodniczych i społecznych interakcjach. W pracy przedstawiono również krytyczne poglądy na współczesne rolnictwo i nawożenie, a także wskazano, że właściwe stosowanie nawozów sztucznych jest i powinno być ważnym czynnikiem produktywności roślin uprawnych. W pracy przedstawiono także najbardziej podstawowe nawozy sztuczne i współczesny poziom zużycia składników nawozowych w Polsce. Tytuł pracy, który jest również główną tezą opracowania, w pełni potwierdza prawdziwość tego poglądu, że nawozy sztuczne nie są, ani szkodliwe, ani toksyczne i to jest przeciwieństwem do powszechnych i fałszywych opinii, które straszą nawozami jako niebezpiecznymi dla ludzi co jest oczywiście w pełni bezpodstawne.

Słowa kluczowe: definicja rolnictwa, nawozy sztuczne, krytyka nawożenia

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THE CONTENT OF SELECTED PHOSPHORUS FORMS IN PARTIALLY ACIDULATED PHOSPHATE ROCKS ENRICHED WITH SULFUR

BADANIE ZAWARTOŚCI WYBRANYCH FORM FOSFORU W FOSFORYTACH CZĘŚCIOWO ROZŁOŻONYCH WZBOGACONYCH W SIARKĘ

Abstract: Sulfur enrichment becomes emerging issue in fertilizer production as levels of available compounds decrease over the years. Companies are in need of exact parameters and methods of enrichment. In this group PAPR-type fertilizers with this element are interesting solution. Specific technology of PAPRs production consists of phosphate rock acidulation with non-stoichiometric, in relation to production of superphosphates, amount of mineral acid (mainly orthophosphoric or sulfuric acids). Additional function of S after applying fertilizer to soil can be used in this. S in product made that way can be, after the process of mineralization, used by plants as a nutrient in form of sulfate ion SO_4^{2-}, additionally it can act as an increasing factor in the phosphorus availability from PAPRs. In an optimal conditions (pH ~6.0–6.8) SO_4^{2-} ions can activate conversion of undissolved part of fluorapatite ($Ca_5(PO_4)_3F$), contained in phosphate rock, to available $H_2PO_4^-$ and HPO_4^{2-} phosphate ions. The aim of this research was the evaluation of contents of selected phosphorus forms in PAPR-type fertilizer enriched with S depending on a various methods of enrichment. The obtained products were characterized by constant ratio of S : P_2O_5 (1 : 1 w/w), value of degree of PAPR stoichiometric norm ($\eta_{PAPR} = 0.5$), constant amount of surfactant (5 cm^3) and variable humidity, which was achieved by different amounts of water introduced into the system (0, 15, 35 % w/w). Method with less additional H_2O (~15 % m/m) and surfactant added to slurry was selected for further studies. Although the best solution for industrial manufacturing might be the method with melted S, where usage of this medium and temperatures of 140 °C are easily achievable and facilitates production without adding dispensable water, which has a negative influence on granulation process. Next step was to study sulfur effect on PAPRs based on phosphoric acid enriched with sulfur using chosen method. Results revealed that $\eta_{PAPR} = 0.5$ is unaffected by addition of sulfur and might be best for mixing with sulfur-based fertilizers. Furthermore $\eta_{PAPR} = 0.7$ indicated decreases in P forms with addition of excessive amounts of elemental sulfur.

Keywords: phosphate fertilizers, partially acidulated phosphate rocks (PAPR), elemental sulfur, available phosphorus

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Introduction

Poland after joining the EU was obliged to fulfill standards in field of environmental protection. From base year 1988 total emission of sulfur dioxide (SO_2) to the atmosphere was reduced to 861 thousand Mg in year 2009, where years 2000–2009 noted 43 % reduction [1]. Reduced flow of SO_2 from main sources *ie* stationary, power engineering, industrial power engineering (correspondingly: 39.3; 37.5; 20.7 %) with simultaneously restricted use of fertilizers containing this element, caused, in late 90's of last century, degradation of available sulfur supply in soil and in plants [2].

In soil sulfur occurs in organic forms (amino acids: cysteine and methionine, deciding on biological properties of proteins), in turn direct sources of S available are only inorganic sulfates [3, 4]. Organic P must be converted to inorganic P through a relatively slow mineralization process before it becomes available, organic fertilizers may not meet plants' early P requirements often resulting in lower crop yield [5, 6]. In order to supplement deficiency of SO_4^{2-} ions in soil, the mineral fertilizers enriched with S are used preferably. These are mainly sulfate fertilizers which are main source of this component: ammonium sulfate, single superphosphate, potassium sulfate or gypsum [7]. Unlike conventional N fertilizers which are all water soluble, P fertilizers vary widely in solubility that can influence the initial and residual P effects. For this and other reasons, inorganic P fertilizers remain the major sources of P application used by farmers in both developed and developing countries [5, 8]. Interesting product in this group are PAPR-type (*Partially Acidulated Phosphate Rock*) fertilizers enriched with S. Specific production technology of PAPR-type fertilizers is based on dissolution of phosphate raw materials (mainly phosphate rocks) by non-stoichiometric amount of mineral acids (mainly sulfuric acid, ortophosphoric or mixture of those). It enables tapping additional function of sulfur after applying fertilizer product to soil [9]. In PAPR technology, beside water soluble $Ca(H_2PO_4)_2$, calcium sulfate is created (source of SO_4^{2-}) – important source of S, which is supplemented by elementary sulfur [10]. Elementary sulfur in this fertilizer system, after mineralization process (optimal conditions: pH ~6.0–7,0; humidity ~60 %, temp. 20–30 ^{o}C) can be used by plants as nutrient in form of SO_4^{2-} ion. Additionally intensifying phosphorus solubility from PAPR-type fertilizer. In optimal conditions (pH ~6.0–6.8) SO_4^{2-} ions can activate conversion of undissolved fraction of $Ca_5(PO_4)_3F$ from phosphate rock to available phosphate ions $H_2PO_4^-$ and HPO_4^{2-} [11–13].

Important factor in industrial methods of sulfur enrichment is optimization of process parameters to intermediate product by economic and ecological reasons. Significant problem of sulfur is flammable dusts emission which occurs during grinding process in order to obtain fine particles. Another factor is the water added in slurry with sulfur, making granulation process more expensive due to increased humidity. Mineralization process comes with lower pH of the soil. Soil's pH, fertilized by the product is one of the main reasons deciding on heavy metals availability to plants. Lowering pH to acidic increases mobility of the available heavy metals forms concentration and increases their accumulation in plants. It is caused by increased solubility and lower absorption on soil colloids.

Materials and methods

The purpose of the research was to determine impact of methods of adding sulfur to fertilizer products on selected P forms in PAPR-type fertilizers obtained in laboratory scale. Parameters which were modified were as follows:

– method of adding sulfur: in slurry with water; melted sulfur,
– percentage of water added to the reactor (0 – none, 15, 35 % w/w),
– percentage of surfactant added to the reactor (0 – none, 2.3, 3.0, 3.5 % w/w).

Table 1

Matrix of the experiment

Fertilizer PAPR product	ZIN weighed portion [g]	S : P_2O_5 ratio [w/w]	H_2O added to the reactor [% w/w]	Surfactant added to the reactor [% w/w]	Method of adding sulfur
1	100	1 : 1	35	2.3 (5 cm^3)	Sulfur water slurry Surfactant added to slurry
2			15	3.0 (5 cm^3)	Sulfur water slurry Surfactant added to slurry
3			35	0	Sulfur water slurry
4			0	0	Melted sulfur
5			0	3.5 (5 cm^3)	Melted sulfur Surfactant added to slurry
6			0	0	Control sample: PAPR 0.5 without sulfur

Israeli “ZIN” phosphate rock was used in the research for which constant degree of PAPR stoichiometric norm $\eta_{PAPR} = 0.5$ was applied. Rate of S : P_2O_5 was established at 1:1 (w/w) with constant value throughout the investigations. Selected forms of P were analyzed using methods in the Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilizers, and Polish standard PN-88C-87015 – Mineral Fertilizers, Methods of phosphate content determination [10, 14]. PAPRs were obtained in modular ATLAS batch reactor (Syrris Ltd.) using overhead stirrer RW 28 basic (IKA®-Werke GmbH&Co. KG) to ensure efficient homogenization taking into account the resistance of pulp solidifying in the reactor. The apparatus applied during investigations allowed the batch type production process. To ensure sufficient sulfur diffusion “Superplasticizer CA40 FF” (Liquid solution of calcium naphthalenesulphonates condensed with formaldehyde) was used provided by PCC Rokita S.A. In second method sulfur was introduced to the reactor and then heated up to 140 ^{o}C and mixed at 50 rpm. After the process product was dried on air and analyzed.

Further research was made to determine impact of sulfur on PAPR-type fertilizers based on phosphoric acid. Method of enrichment was based on adding elemental sulfur as slurry with water as described above (Product No. 2). Constant S : H_2O ratio was established at 1 : 1 (w/w). Analysis was made on the day of production and consecutively week and two later. Parameters which were modified were:

- Degree of PAPR stoichiometric norm (η_{PAPR} = 0.3, 0.5, 0.7),
- S : P_2O_5 ratio (w/w) (1:2; 1:3; 1:4; 1:6).

Table 2

Matrix of the experiment

Fertilizer PAPR product	ZIN weighed portion [g]	PAPR norm	S : P_2O_5 ratio	H_2O added to reactor [% w/w]	Surfactant added to reactor [% w/w]
D1	100	0.3	1:2	8.88	3.51
D2			1:3	6.29	3.73
D3			1:4	4.87	3.86
D4			1:6	3.35	3.99
E1		0.5	1:2	7.82	3.10
E2			1:3	5.51	3.27
E3			1:4	4.24	3.36
E4			1:6	2.91	3.46
F1		0.7	1:2	7.00	2.77
F2			1:3	4.89	2.90
F3			1:4	3.76	2.98
F4			1:6	2.57	3.05

Results and discussion

Results of the selected phosphorus forms in PAPR-type fertilizers enriched with sulfur analysis are shown in the Table 3.

Table 3

Results of various forms of P analysis in the investigated products expressed as % P_2O_5 (w/w)

Product	P soluble in mineral acids [% w/w]	P soluble in citric acid 2 % [% w/w]	P soluble in neutral ammonium citrate [% w/w]	P soluble in formic acid 2 % [% w/w]	Water-soluble P [% w/w]
1	18.68	13.21	9.98	12.98	6.76
2	19.20	10.71	10.15	11.03	5.98
3	25.07	13.25	9.26	13.00	8.13
4	19.79	6.50	7.01	5.78	3.87
5	21.19	9.21	7.09	7.79	6.13
Control sample PAPR 0.5 without sulfur	24.15	11.83	9.92	11.99	8.36

Product No. 3 revealed the highest amount of available phosphorus forms (P soluble in H_2O : 8.13 %), however in this case, the applied method did not assure sufficient diffusion of sulfur in fertilizer product and requires adding additional amount of water which has adverse influence on granulation process. Fertilizer products obtained by methods with melted sulfur contained least amounts of soluble phosphorus forms (correspondingly 3.87 and 6.13 % for water-soluble P). This might be connected to high temperature of the process which degrades soluble forms into insoluble. In the laboratory research method according to product No. 2 was selected for further studies, where humidity is lower and diffusion sufficient. Worth noting is that better for industrial manufacturing might be method based on melting sulfur because temperature of 140 ^{o}C is easily achievable and sulfur handling is relatively safe without the need of adding dispensable water.

Results of further research were shown in Table 4.

Table 4

Results of various forms of P analysis in the PAPRs enriched with sulfur expressed as % P_2O_5 (w/w)

Product	Fertilizer growth [days]	P soluble in mineral acids [% w/w]	P soluble in citric acid [% w/w]	P soluble in formic acid 2 % [% w/w]
D1	0	32.84	18.62	20.07
	7	29.69	17.19	17.71
	14	32.12	19.36	19.36
D2	0	28.29	17.09	19.83
	7	31.69	16.26	17.37
	14	32.92	17.44	18.89
D3	0	30.49	16.48	18.22
	7	31.37	15.60	16.29
	14	33.26	15.70	16.37
D4	0	31.49	16.77	19.24
	7	31.64	17.05	17.60
	14	34.52	18.46	17.79
E1	0	32.78	26.18	23.14
	7	32.13	22.34	23.39
	14	34.84	23.90	24.46
E2	0	34.62	22.39	23.87
	7	32.24	22.59	22.87
	14	36.89	24.35	23.32
E3	0	36.19	24.68	25.32
	7	33.73	23.40	24.25
	14	34.65	23.73	23.71
E4	0	37.44	25.16	26.41
	7	34.04	22.94	23.47
	14	35.52	23.61	24.01

Table 4 contd.

Product	Fertilizer growth [days]	P soluble in mineral acids [% w/w]	P soluble in citric acid [% w/w]	P soluble in formic acid 2 % [% w/w]
F1	0	35.25	26.31	28.43
	7	34.70	26.36	26.66
	14	33.77	26.12	26.43
F2	0	35.45	28.22	29.25
	7	34.32	27.23	27.11
	14	34.69	28.18	28.43
F3	0	37.34	32.67	32.46
	7	37.45	25.23	29.60
	14	35.55	30.70	31.86
F4	0	38.11	32.56	31.77
	7	37.94	30.87	30.91
	14	38.44	31.45	32.29

Fertilizer products of the degree of PAPR stoichiometric norm at 0.3 (D series products) were characterized by increased contents in selected phosphorus forms along with increasing amount of sulfur (difference being 1 % w/w for water-soluble P). This might be accounted for further dissolution of phosphate rock by sulfuric acid obtained from oxidized elemental sulfur. In turn products of the degree of PAPR stoichiometric norm at 0.3 (F series products) noted inversed correlation. Increase of S to enriched PAPR-type fertilizers resulted in decrease of contents of selected P forms (difference about 6 % w/w for water-soluble P). This might be due to high amount of phosphoric acid which favors elemental sulfur form rather than oxidized. Degree of PAPR

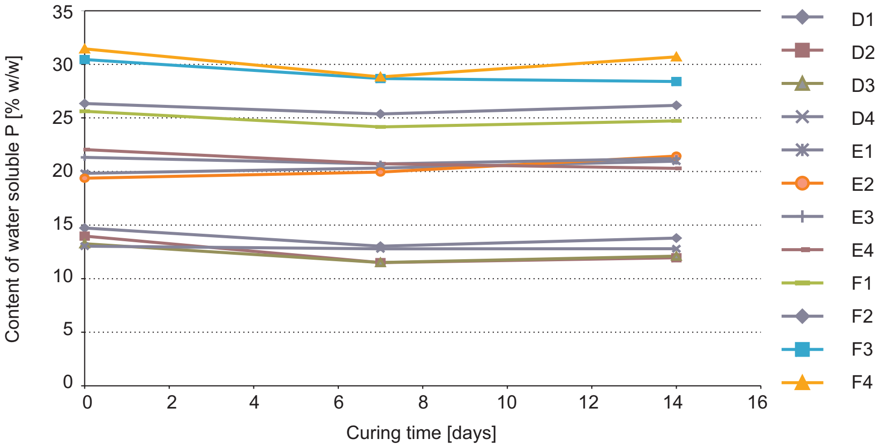

Fig. 1. Results of water soluble forms of P analysis in PAPR-type fertilizer products enriched with sulfur expressed as % P_2O_5 [w/w]

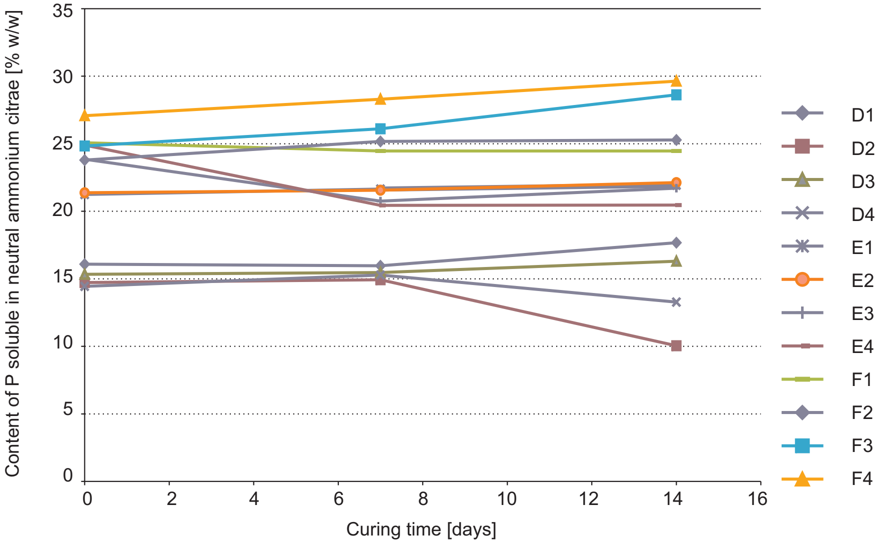

Fig. 2. Results of neutral ammonium citrate soluble forms of P analysis in PAPR-type fertilizer products enriched with sulfur expressed as % P_2O_5 [w/w]

stoichiometric norm at 0.5 (E series products) indicates similarity to 0.3 value in higher S : P_2O_5 ratios (1 : 2; 1 : 3), corresponding to 0.7 when considering lower ratios (1 : 4; 1 : 6). This would confirm the authenticity of previous trends and speculations of what causes them.

Conclusions

The best method of enrichment is adding sulfur in slurry with water and surfactant. It ensures sufficient diffusion and allows usage of decreased amount of water (15 instead of 35 % w/w) which has negative influence on granulation process. Addition of water is important factor in decreasing the soluble forms, but surplus increases insoluble forms. Usage of slurry greatly reduces dangers of working with sulfur and makes handling easier. The content of phosphorus forms soluble in water and/or neutral ammonium citrate is satisfactory. Worth noting is that better for industrial production might be method based on melting sulfur (product No. 5) where handling this medium is easy and no dispensable water is used in manufacturing process. However this method reduces content of phosphorus forms soluble in water and/or neutral ammonium citrate. Addition of sulfur in PAPR-type fertilizers based on phosphoric acid is most effective in case of degree of PAPR stoichiometric norm at $\eta_{PAPR} = 0.3$, where higher amounts of sulfur in product boosts content of phosphorus, especially in the available forms (4 % increase for neutral ammonium citrate and 1 % increase for water-soluble forms). Lower ratios are more effective for the degree of PAPR stoichiometric norm at $\eta_{PAPR} = 0.7$ (5 % increase for neutral ammonium citrate and 6 % for water-soluble forms). For the degree of PAPR stoichiometric norm at $\eta_{PAPR} = 0.5$ results imply that sulfur has no effect on P forms. It allows mixing with sulfur-based or sulfur enriched fertilizers without decrease in P content. Taking into consideration industrial conditions, where superphosphate constitutes the primary product (degree of PAPR stoichiometric norm at $\eta_{PAPR} = 1.0$) we can predict lower ratios being most effective (phosphorus content-wise). This also influences lower humidity (decreased amount of dispensable water added from 7.00 to 2.57 %) which makes it more economical than higher ratios, at least when using slurry method.

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BADANIE ZAWARTOŚCI WYBRANYCH FORM FOSFORU W FOSFORYTACH CZĘŚCIOWO ROZŁOŻONYCH WZBOGACONYCH W SIARKĘ

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Abstrakt: Wzbogacanie nawozów mineralnych siarką elementarną staje się coraz bardziej widocznym problemem dla przemysłu nawozowego. Zakłady produkcyjne potrzebują specyficznych metod i parametrów procesu dodawania siarki. W tej grupie interesującym produktem są nawozy typu PAPR (*Partially Acidulated Phosphate Rock*). Specyficzna technologia produkcji nawozów PAPR polegająca na rozkładzie surowców fosforowych (głównie fosforytów) niestechiometryczną, względem reakcji wytwarzania superfosfatów, ilością kwasów mineralnych (głównie siarkowym lub fosforowym) pozwala na wykorzystanie dodatkowej funkcji siarki po aplikacji nawozu do gleby. S w tak przygotowanym układzie nawozowym może po uprzednim procesie mineralizacji (warunki optymalne: pH ~6,0–7,0; wilgotność ~60 %, temp. 20–30 ^{o}C) zostać wykorzystana przez rośliny jako składnik odżywczy w postaci jonu siarczanowego SO_4^{2-}, a dodatkowo działać jako czynnik intensyfikujący przyswajalność fosforu z nawozu PAPR. W optymalnych warunkach (pH ~6,0 – 6,8) jony SO_4^{2-} mogą aktywować konwersję nierozłożonej frakcji fluoroapatytu ($Ca_5(PO_4)_3F$) zawartego w surowcu fosforowym do przyswajalnych jonów fosforanowych w formie $H_2PO_4^-$ i HPO_4^{2-}. Celem niniejszych badań była ocena zawartości poszczególnych form fosforu nawozów PAPR wzbogaconych w siarkę, uwzględniając różne metody wzbogacania. Analizy zawartości poszczególnych form P przeprowadzono metodyką analityczną zgodną z dyrektywą Wspólnoty Europejskiej w sprawie nawozów oraz z procedurami zawartymi w polskich normach. Otrzymane preparaty charakteryzujące się stałym stosunkiem S : P_2O_5 (1 : 1 m/m), wartością stopnia normy stechiometrycznej PAPR ($\eta_{PAPR} = 0,5$), oraz zmienną wilgotnością, co osiągnięto poprzez zmienne ilości wody wprowadzanej do układu (0, 15, 35 % m/m), uzyskiwały najwyższe zawartości przyswajalnych form P (P rozpuszczalny w wodzie: 8,13 % P_2O_5 m/m, P rozpuszczalny w obojętnym cytrynianie amonu: 10,15 % P_2O_5 m/m) dla metody dodawania siarki w postaci zawiesiny wodnej bez dodatku surfaktantu (H_2O ~35 % m/m). Do dalszych badań laboratoryjnych wybrano metodę produkcji, gdzie dodatek H_2O jest niższy (~15 % m/m), a surfaktant wprowadzony do zawiesiny wodnej S. Metoda stapiania S może być najlepsza do produkcji przemysłowej, gdzie stosowanie stopionej S lub temperatury rzędu 140 °C zostało opanowane w stopniu znacznie ułatwiającym produkcję bez dodawania zbędnej zawartości wody mającej niekorzystny wpływ na proces granulacji. Kolejnym krokiem było określenie wpływu zawartości siarki na produkty nawozowe typu PAPR wytworzone z zastosowaniem kwasu fosforowego wzbogaconego w siarkę elementarną, bazując na wybranej metodzie. Wyniki wykazały, że produkty o $\eta_{PAPR} = 0,5$ nie są znacząco podatne na wprowadzenie siarki elementarnej do składu nawozu, co może być przydatne podczas komponowania mieszanek nawozów wieloskładnikowych. Ponadto dla produktów nawozowych typu PAPR o $\eta_{PAPR} = 0,7$ wykazano tendencje spadkowe rozpuszczalnych form P wraz z zastosowaniem wyższych zawartości siarki elementarnej.

Słowa kluczowe: nawozy fosforowe, fosforyty częściowo rozłożone (PAPR), siarka elementarna, fosfor przyswajalny

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MIGRATION OF PAHs IN THE ARABLE LAYER OF FLOODED SOIL – MODEL EXPERIMENT

MIGRACJA WWA W WARSTWIE ORNEJ GLEB ZALANYCH WODAMI POWODZIOWYMI – DOŚWIADCZENIE MODELOWE

Abstract: Soils periodically, or permanently, waterlogged and soils exposed to flood waters are heavily imperilled to pollution of inorganic and organic compounds. They are primarily compounds that are brought with the inflowing (highly loaded) floodwater and indigenously produced within the soil profile by anaerobic metabolism of the organic matter. PAHs compounds are adsorbed by the soil from the floodwaters and move in the soil profile posing a threat to groundwater. In addition, when the flood recedes, these compounds may be taken up by the crops. In this study soil pollution with polycyclic aromatic hydrocarbons (PAHs) derived from the decomposition of organic matter and silt and their migration in the arable layer of soil.

Keywords: flood, PAHs, soil, migration of pollutants

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs), due to their toxicity, mutagenicity and carcinogenicity constitute persistent organic pollutants of the environment [1–3]. They are formed through natural processes (volcanic eruptions, forest fires, decomposition of biomass) and anthropogenic (industry and transport) [2, 4]. These compounds are emitted into the atmosphere from combustion of various organic materials such as liquid and solid fossil fuels; commonly used as fuel to drive piston engines and within

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the energy sector [1, 2]. A huge number of sources (natural and anthropogenic) create such compounds, along with their considerable dispersion; enable PAHs to be present in all components of the environment [5–9]. PAHs are nonpolar and aromatic compounds, therefore are practically insoluble in water, but in the presence of other organic impurities their solubility may increase. Due to their high affinity to the solids, they may adsorb onto the surface of the particles and, then with them can move over large distances. Along with rainwater PAHs are absorbed on particulates and washed away from the surface of roads, parking lots, rooftops, warehouses, petrol stations, places of storage of solvents, pesticides, landfills and both get into the soil and hence into the soil profile and groundwater. In the surface reservoirs these compounds settle at the bottom, accumulating in sediments. Some of PAHs are degraded over time (weeks, months) by various groups of microorganisms, and the others may further accumulate in the food chain. PAHs are collected by the plants through the roots, and then moved to the aerial parts [10].

Long-term rainfall and rapid thaw lead to raised water stage in rivers, resulting in deluge or flood, resulting in long-term negative effects on the environment. Flooded soil sustaining even for a short time, leads to a displacement of air from the soil pores what results in formation of anaerobic conditions in their profile. Such a situation may be the case for all types of soils [11].

Pollutants that are carried along with the floodwater can be divided into two main groups. The first group consists of inorganic compounds which include, amongst others, heavy metals and nutrients, which migrate into the soil profile and are stopped on the physical, biological or chemical sorption processes [3]. The second group are the previously mentioned organic compounds that are the building blocks of pre-decomposed plant and animal residues as well as organic matter of different origins. These are originally contained in the soil, compost and manure coming from the manure, liquid manure tanks and finally septic tanks. Furthermore, the floodwaters contain organic compounds that may have toxic properties, for example: substances purifying lubricants or having irritant nature such as alcohols, hydrocarbons, including aliphatic and monoaromatic [12]. In the floodwaters-eluting everything in its path there are organic compounds belonging to the so-called "persistent organic pollutants" (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins, polychlorinated dibenzofurans (PCDD and PCDF) and polychlorinated bi- and terphenyls (PCBs and PCTs) [13]. In periods when there is no flooding, soil is also exposed (although to a much lesser extent) persistent organic pollutants (including PAHs) as a result of dry deposition precipitation.

The group PAHs' include more than 200 compounds, however, for the monitoring purposes 16 were chosen that were characterized by particularly toxic (carcinogenic and mutagenic) properties. These compounds are characterized by the so-called chronic toxicity, which means that the dose is harmful in the case of prolonged exposure [14].

Not only the floodwaters but also dry deposition precipitation may bring significant quantities of metals and POPs [9, 14]. Also, organic fertilization with manure or slurry, compost, and especially sewage sludge constitutes a process of "enriching" the soil not only in organic substances necessary for its cultivation, but also redundant organic substances such as polycyclic hydrocarbons [16–20]. Number of noted compounds of PAHs in soils accelerate anaerobic conditions (as a result of fermentation of organic matter in the soil) often occurring with high groundwater levels, particularly during flooding, when the waters cover the soil for a long period of time [21]. Allochtonous compounds of PAHs that are getting into the soil are absorbed mainly in the humus layer [22]. Organic matters present in amounts above 0.1 % are largely responsible for the sorption of pollutants [23]. However, the compounds of PAHs, despite a relatively low solubility in water due to the accompanying substances, may migrate along the direction of water flow into the profile and can then be collected by plants or got into the aquifers causing contamination, particularly strong in the case of light soils [22, 24]. Interaction of PAHs depends not only on the sensitivity of the body, but mainly on the type and concentration of the compound, and the coexistence of the other PAH compounds of the group. It has been shown that pyrene enhances the damaging effects benzo[a]pyrene. The group of the most carcinogenic properties include benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[b]fluoranthene [14].

The article focuses on the results of a study simulating flooding. The study also evaluated the rate of migration of PAHs in light soils that was subjected to a short process of flooding completely covering the area as a factor that may eliminate the soil from cultivating intended for direct consumption.

Materials and methods

The experiment used soil samples (type: mud river) from arable layer, with grain size characteristic for loamy soils. Before the experiment, the soil was dried at room temperature and sieved through a 2 mm diameter mesh.

The ash was obtained from the incineration of oak biomass in an open small furnace, and was then incinerated at 600 ^{o}C for 2 hours for small of uncompleatly burned particles removal and then sieved through a sieve with a mesh diameter of 2mm. For experimental purposes, the amount of fertilization used is 5.52 Mg to ash/ha (GP), what was calculated on the base standard amount of mineral fertilizing 2Mg CaO / ha. The same soil without the ash (series G) was used as a reference sample. The test soil was placed in a glass cylinder with dimensions of 3 × 15 cm (106 cm^3). Then on the surface of the soil in the cylinder, some “flood sediment” was placed containing heavy metals in amount of 2.00 g/cylinder. The “flood sediment” was made by mixing in a 1:1:1 ratio (m/m) of sapropel sediment derived from the dam reservoir Turawskie Large Lake, of LRM1 certified reference material (Gdansk University of Technology, Poland) and a certified reference material LRM-CC013a (BAM, Berlin, Germany). For the simulation of fine-grain flood sediment, the sediment, before it was used, was thoroughly ground in an agate mill and sieved through a sieve with a mesh diameter of 0.5 mm. The cylinder’s edges were secured with quartz wool. Cylinders were filled completely using the rainwater with capillary ascension method and incubated in the dark at a constant temperature of 22 ± 0.2 ^{o}C for a period of 7 days. On 7th day after filling, the water was removed. Then, simulating the precipitation, cylinders with soil were washed with rain water in amount of 30mm/week , and the analysis of metals in the soil cores were made on days 7th, 14th, 28th and 42nd after filling the cylinders. After removing the soil from the core glass cylinder, it was separated for analysis into sections a, b, c and d corresponding to depths 0–3, 3–6, 6–9 and 9–12 cm profile, in order to capture the metal penetration into the deeper layers of soil.

However Regulation of Polish Ministers of Environment (9 September 2002) according to soil standards (Regulation MOE 165) recommend for determination only 9 compounds from PAHs group, in this work were collected data about 16 compounds specified on US-EPA list [25]. In investigated samples were determined also: reaction (pH), EC, organic matter content, TOC (with methods specified in Polish Standards). Heavy metals (Zn, Cu, Cr, Ni, Pb, Cd, Mn) were determined in averaged samples for each segment, by taking 4 independent samples from the tested core layer. In addition, the following parameters in the soils were determined: pH, electrolytic conductivity (EC), the content of organic matter and organic carbon (methodology according to Polish Standards). The content of calcium, sodium, potassium and lithium was ascertained in wet mineralizates by FES method using BWB-XP apparatus. The content of the other analysed metals (Zn, Cu, Cr, Ni, Pb, Cd, Mn) was determined by using a spectrophotometer Thermo AAS iCE 3500 after wet microwave assisted mineralization in aqua regia using MARS-X device. Polycyclic aromatic hydrocarbons analysis was carried out in a few steps. First of all fresh samples were dried at room temperature with anhydrous sodium sulphate (POCH) [26]. Extraction was carried out by a DCM-hexane (GC-grade) mixture in a ratio of 1:9 (v/v) in extraction device fexIKA® [15, 19, 22]. Before GC analysis, the extracts were purified by aluminium oxide (Aldrich) on glass columns [27]. Inspissated elutes were analysed by a GC-MS method (Shimadzu GC 17A with MS-QP5000) on capillary column VF5-ms 60 m; ID 0.25 mm and if 0.25 μm. The temperature of the chromatograph injector was 300 ^{o}C while the detector was 320 ^{o}C. The oven temperature program: 80 ^{o}C – 8 minutes, heating 10 ^{o}C/min to 270 ^{o}C, heating 2 ^{o}C/min to 300 ^{o}C. Detector current 1.2 to 1.4 kV In each sample 16 single compounds were determined which are recommended for monitoring by U.S. Environmental Protection Agency (US-EPA): naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenantrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (B[a]ant), chrysene (Chr), benzo[b]fluoranthene (B[b]flt), benzo[k]fluoranthene (B[k]flt), benzo[a]pyrene (B[a]p), dibenzo[a,h]anthracene (D[a,h]ant), indeno[1,2,3-c,d]pyrene (Ind[123]P), benzo[g,h,i]perylene (B[ghi]per). The flow of a carrier gas (He) was adjusted to 1 cm^3/min. Certified PAHs standards (US-106N 2000 $\mu\mathrm{g} \cdot \mathrm{cm}^{-3}$ of each compound; Ultra Scientific USA) were used in order to determine calibration curve. Recovery levels for this procedure were low for naphthalene (57–66 %), and higher (73–92 %) for the rest individual PAHs. Recovery procedure was based on dry samples of PAHs reference materials: "ERM-CC013a" (BAM, Berlin, Germany) and "LRM soil 1" (University of Technology, Gdansk, Poland). The detection limits ranged between 0.05–0.1 μg/kg d.m. for particular PAHs. The uncertainly of the results was calculated as standard deviation value. In order to single out the petrogenic compounds, the PAHs content: ANT/(ANT + PHE), BaA/(BaA + CHR), FLA/(FLA + PYR) in liquid and solid fuel combustion were calculated.

Results and discussion

The analysed soils, before they were poured, differed in terms of physic-chemical parameters (Table 1). The use of ash from biomass in an amount corresponding to liming in a dose 2 Mg CaO/ha resulted in increasing the acidity by 0.74 degree and conductivity of the soil by more than 80 μS/cm.

Table 1

Characteristic of biomass ash (P) experimental soils (G, GP) and "flood sediment" (N) (n = 3)

Parameter	P	G	GP	N	Regulation MOE 165 [25]
Reaction [pH]	11.47(0.01)	6.62(0.01)	7.36(0.01)	7.05(0.01)	—
EC [$\mu S \cdot cm^{-1}$]	12130 (26)	93.4(5.6)	176.8(4.0)	1378(7.8)	—
Organic matter [% d.m.]	0.63(0.09)	3.11(0.22)	3.28(0.02)	8.02(0.22)	—
TOC [% d.m.]	0.02(0.00)	1.01(0.06)	1.02(0.05)	3.27(0.11)	—
CaO [% d.m.]	34.37	0.039	0.049	0.667	—
Na_2O [% d.m.]	0.198	0.004	0.006	0.113	—
K_2O [% d.m.]	8.217	0.094	0.164	0.332	—
Zn [$mg \cdot kg^{-1}$ d.m.]	506.8	59.51	55.59	919.0	300
Cu [$mg \cdot kg^{-1}$ d.m.]	119.6	4.4	4.39	81.41	150
Pb [$mg \cdot kg^{-1}$ d.m.]	21.23	13.99	15.07	70.79	100
Cr [$mg \cdot kg^{-1}$ d.m.]	21.81	4.40	5.13	32.14	150
Cd [$mg \cdot kg^{-1}$ d.m.]	2.27	< 0.2	< 0.2	17.07	4
Ni [$mg \cdot kg^{-1}$ d.m.]	22.2	2.46	2.51	22.72	100
Mn [$mg \cdot kg^{-1}$ d.m.]	4544	261.4	332.0	455.9	—

— no regulation limit.

The use of ash from biomass also resulted in a slight increase in the content of heavy metals, except for manganese. Due to its significant content in the ash, over 27 % increase was noted in this element. The prepared slit from flooding was characterized by neutral reaction and relatively high conductivity. It contained more than 8 % organic matter, which is similar to that of the slit from rivers.

PAHs compounds were identified in the studied soil samples also before flooding. The addition of silt with PAHs above 40 [$mg \cdot kg^{-1}$ d.m.] (Table 2) washed with rainwater should become an important source of additional contamination of the soil profile. Larger amounts of PAHs, primarily due to the content of these compounds in the slit – their migration along with soil micro-particles and humus acid molecules, where PAHs are adsorbed, as well as due to the process of anaerobic decomposition of soil organic matter, and the organic matter permeating into the soil from silt. PAH fraction soluble in water is negligible and, usually do not exceed a few percent of the total content [28]. Decomposition of organic matter (and thus the decline in organic carbon) in the flooded soil is a natural phenomenon, which may increase the rate of transport of PAH [29]. Organic matter can slow the movement of these compounds as a result of the sorption or even help to reduce the concentration of these contaminants, as a result of degradation by soil microflora [30]. Also composting process could reduce content of PAHs in soil or sewage sludge [31].

Table 2

PAH's content in experimental soils (G, GP) and "flood sediment" (N) [μg · kg^{-1} d.m.]

Compound	G	GP	N	Regulation MOE 165 [25]
Naph	41.816	40.434	373.63	100
Acy	29.478	35.106	248.09	nl
Ace	36.353	40.434	342.74	nl
Flu	44.264	60.223	432.91	100
Phe	80.429	88.764	4705.2	100
Ant	149.65	156.50	1548.0	nl
Flt	130.25	180.67	6403.5	100
Pyr	129.69	150.79	4694.3	nl
B[a]ant	98.700	111.12	3185.5	100
Chr	156.43	180.57	5834.6	100
B[b]flt	109.34	116.73	2891.6	nl
B[k]flt	151.16	173.53	3531.4	100
B[a]p	76.003	86.957	2192.6	30
Ind[123]p	57.544	89.525	1030.6	nl
D[ah]ant	udl	udl	419.13	nl
B[g,h,i]per	5.180	9.038	2602.8	100
Σ PAH	784.23	931.31	29262	1000
Σ 16 PAH	1296.3	1520.4	40436	nl

udl – under detection limit; nl – no limit value.

The content of the tested 16 compounds from the group of PAHs before the start of the experiment was similar in both series of research (G and GP). Compound whose occurrence was not recorded in the soils was D[ah]ant (Table 2). However, in soil layer group b classified as agricultural land, some exceeding was recorded above the permissible concentrations in the surface layer (0–30 cm) in the case of Flt, B[a]ant, Chr, B[k]flt, and B[a]p. Indicator compound with proven carcinogenic and mutagenic properties is benzo(a)pyrene which permissible content in the soils of this group has been set at 30 μg kg^{-1} d.m. [25]. The calculated ratios of individual compounds in samples G, indicates anthropogenic character (derived mainly from the combustion of liquid and solid fuels) of determined PAHs.

Prepared for experimental purposes flood silt contained significant amounts of the analysed compounds (the amount of 16WWA > 40 mg · kg^{-1} d.m.) and almost 30 times more than the permissible level specified regulations (Regulation MOE 165) and 20 times more than in soils from second-hand car marketplace [25, 32]. So high content of PAHs compounds could effect total toxicity effect for wide number of organisms [33].

Rainwater used in experiment (Table 3) was characterized by a basic reaction, a small electrolytic conductivity and relatively low content of organic matter.

Table 3

Characteristic of rainwater used for flooding experimental cylinders and effluent after 7-day of experiment

Parameter	Rainwater	Effluent G	Effluent GP
pH	8.97	7.25	7.97
EC [$\mu S \cdot cm^{-1}$]	100.4	594	689
COD-Mn [$mgO_2 \cdot dm^{-3}$]	5.8	56.2	76.2

The effluents obtained from the cylinders after 7 days of incubation were characterized with near neutral reaction (G) and slightly alkaline (GP), increased electrolytic conductivity, and a high value of $ChZT_{Mn}$. A higher content of dissolved organic matter (DOM) in the GP series shows intense putrefaction in the cylinders with the addition of ash. This is probably the result of filling the pores of the soil with ash and intensifying degradation as a result of enrichment the solution in the macro- and micronutrients necessary for the proper development of the anaerobic flora. Washed organic matter contains absorbed compounds of PAHs, which with their low solubility in water allows them to migrate into the soil profile, and hence s hould cause higher concentrations of the test compounds than in the control group G [28].

Hydromorphic soils, even unpolluted, may contain higher amounts of PAHs than recorded in prepared for experimental purposes “slit”, reaching even 200–249.6 $mg \cdot kg^{-1}$ in the layer of 0–5 cm [2, 4]. Exposure to periodic inundation by flood water, for example on terraces or flood polders, also increases the amount of PAHs in the soil on those areas in which the value was recorded above 24 $mg \cdot kg^{-1}$ dm for the amount of 19 compounds of this group [23]. The PAH content in the top layer of soil is largely dependent on land use. Urban soils, exposed to pollutants not only communication, but also industrial, contain 5–10 times more PAHs than agricultural soils. This is especially true of 5- and 6-ring compounds [1, 32]. However, pollution from the flood also plays a significant role in the context of the agricultural use of flooded areas. Level Ah soil (0–12 cm) oxbow of the Rhine contained more than 3.6 mg of the sum of 13 PAHs in kg · d.m. [34].

In the experiment there was only a small migration of compounds of PAHs into the profiles of the soils (Fig. 1–15). An increase in concentration in all layers was observed only in the case of Flt and B[ghi]Per, with an average of 110 and 223 %. The nature of migration in both series (G and GP) was similar for the following: Ace, Flu, Ant, for which there were high correlation coefficients at 0.80–0.95 for all layers. In addition, strong correlations (0.77–0.95) were also recorded for B[a]P, Ind[123]P and B[ghi]Per, however, these relationships did not occur in all layers. We did not detect the expected significant increase of concentration of 16 PAHs in layers a and b as a result of the

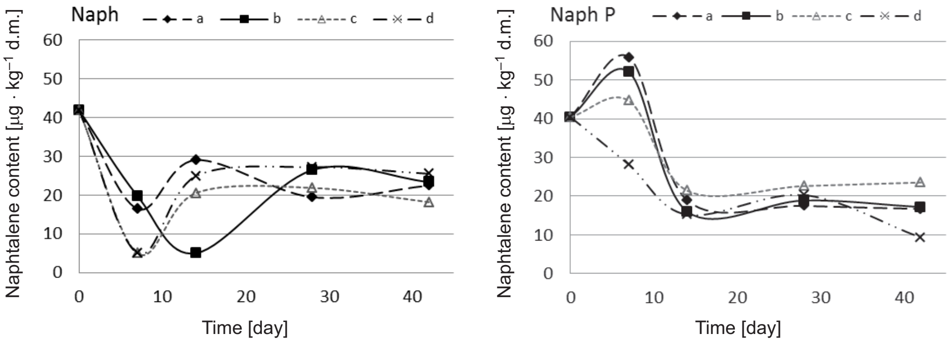

Fig. 1. Naphtalene content changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

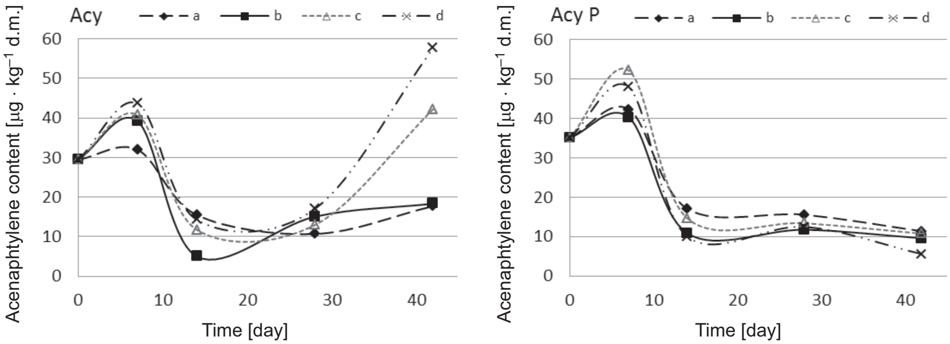

Fig. 2. Acenaphtylene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

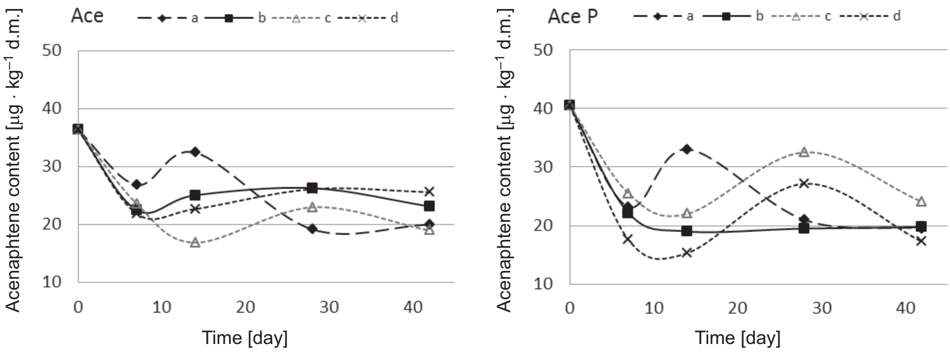

Fig. 3. Acenaphtene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

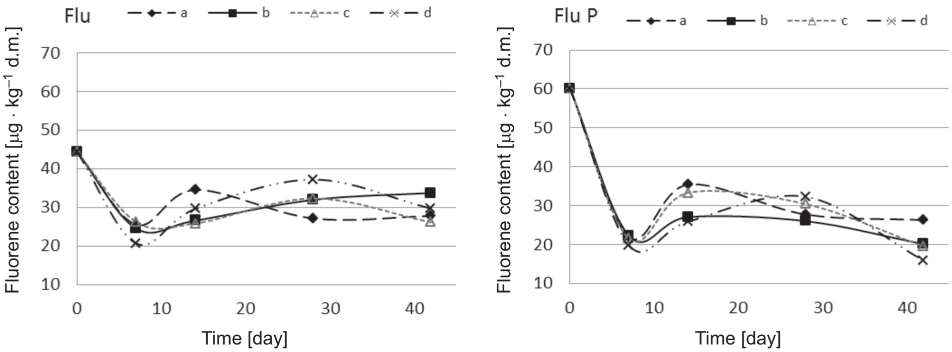

Fig. 4. Fluorene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

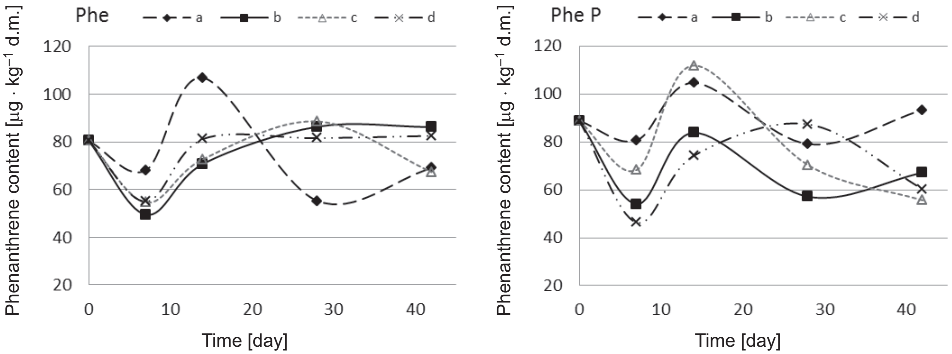

Fig. 5. Phenanthrene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

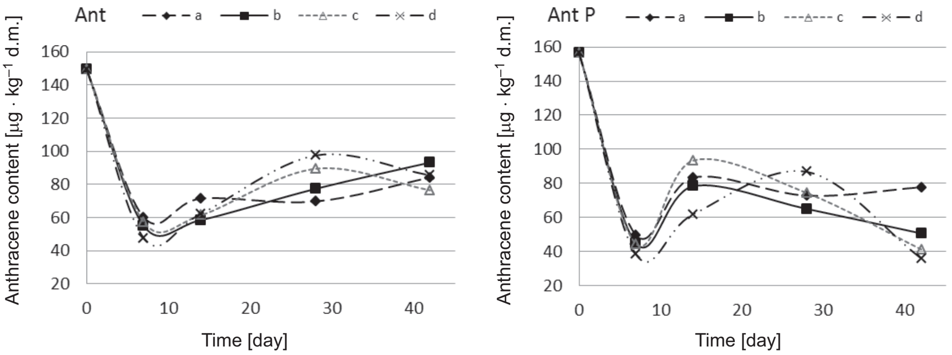

Fig. 6. Anthracene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

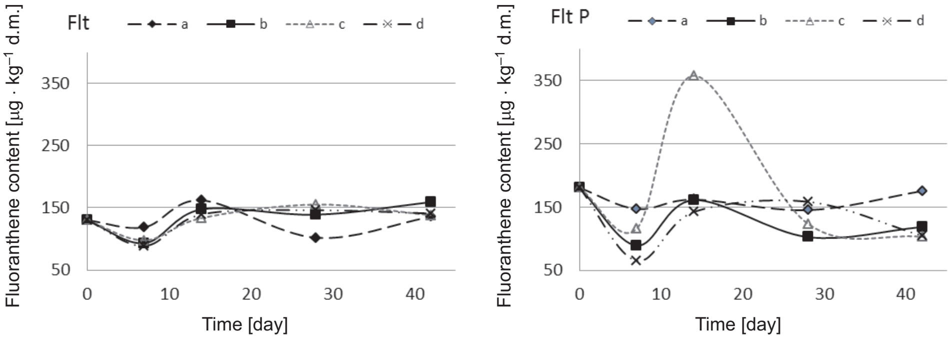

Fig. 7. Fluoranthene content [μg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

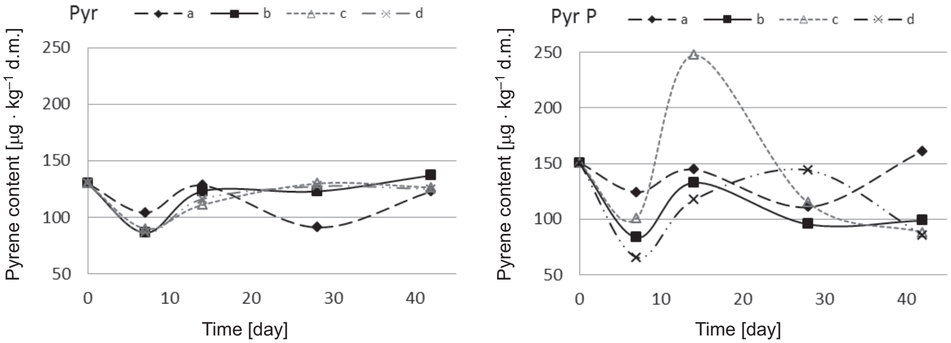

Fig. 8. Pyrene content [μg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

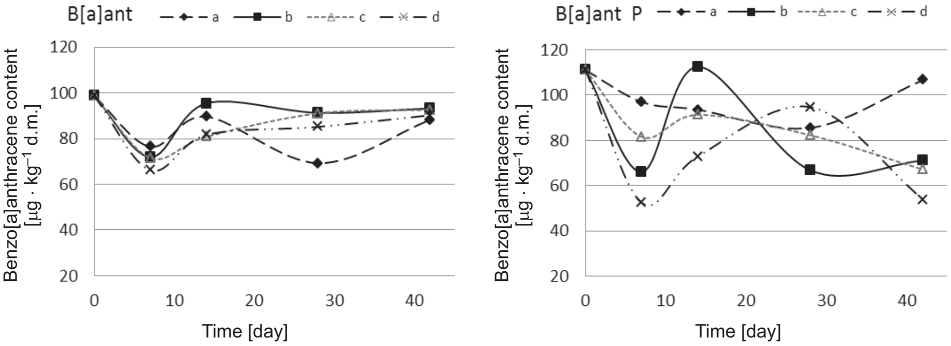

Fig. 9. Benzo[a]anthracene content [μg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

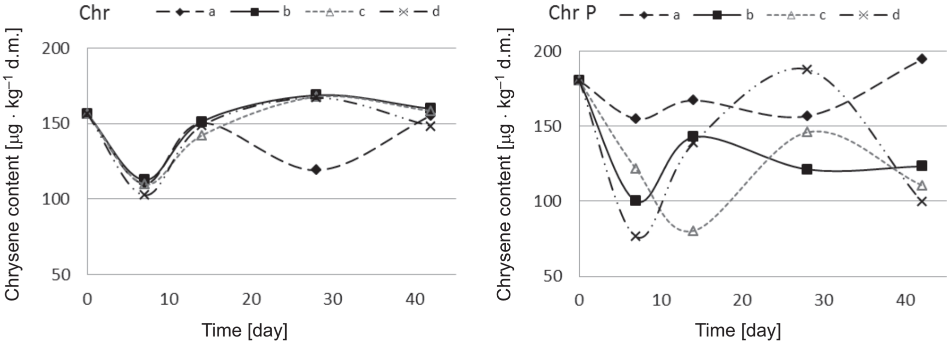

Fig. 10. Chrysene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

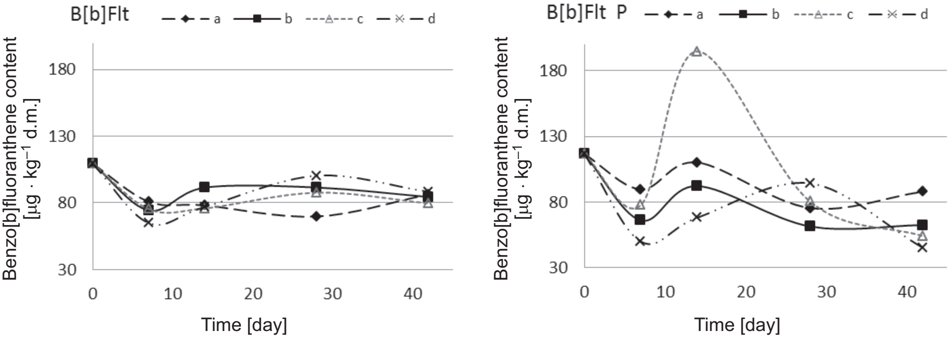

Fig. 11. Benzo[b]fluoranthene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

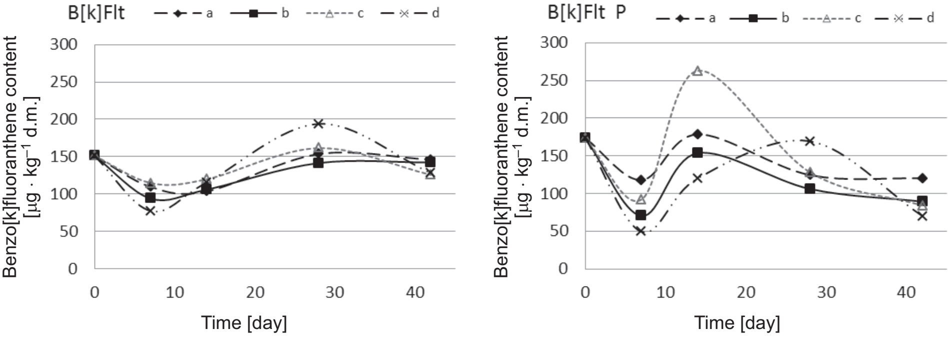

Fig. 12. Benzo[k]fluoranthene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

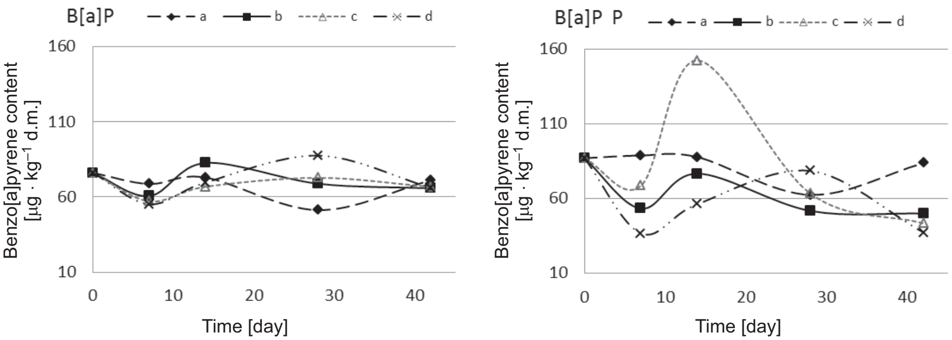

Fig. 13. Benzo[a]pyrene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

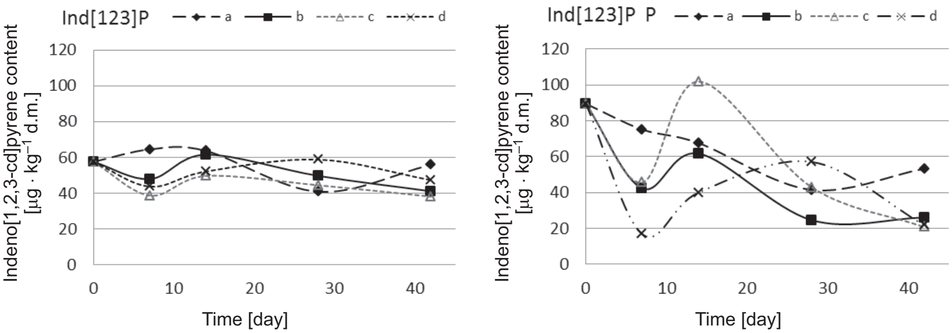

Fig. 14. Indeno[1,2,3-cd]pyrene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

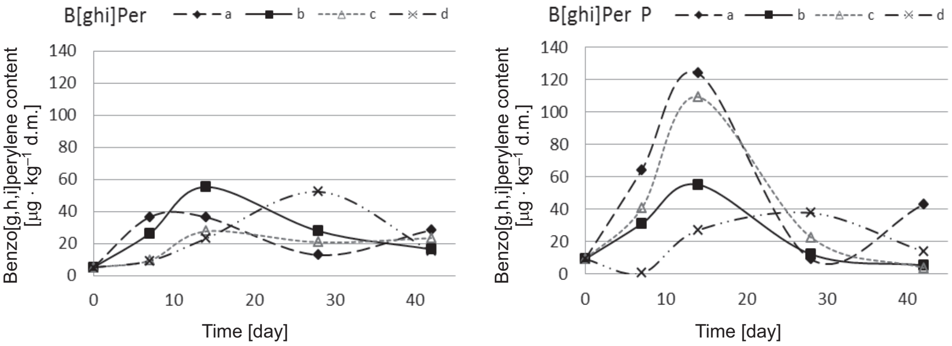

Fig. 15. Benzo[g,h,i]perylene content [µg · kg^{-1} d.m.] changes in control G (left) and experimental GP (right) series, during 42 days model experiment. Experimental layers marked as explained in Materials and methods

migration of silt microparticles by the profiles of the soils. The increase in acenaphthylene on day 7th of the experiment was only recorded for G series and naphthalene and acenaphthylene in a GP series. In the experiment there was observed increased concentrations (light) of 2-, and 3-ring compounds in all layers of the profiles. Moreover, in the GP series an increase of concentrations was noted for Flt, Pyr, Chr, B[b]flt, B[k]flt, B[a]P and Ind[123]P, primarily in the layer "c" on the 14th day.

Analysing the content of PAHs in all studied layers (a–d), a similar distribution of concentrations was observed only for the Ant of G series (corr. coef. 0.91–0.98) and for Acy, Flu, and Ant of GP series (corr. coef. 0.91–0.99).

Moreover, in the GP series, greater volatility of concentrations was observed in the different layers of the profile in relation to small variations recorded in a series of controls (G). In particular, this phenomenon clearly occurred at concentrations of 4- and 6-ring, PAHs that is from Flt to B[ghi]Per.

There was no clear positive correlation between the PAHs concentrations and heavy metals tested, what indicates a different mechanism of migration in the soil. Single correlations for, among others, nickel, zinc and lead with the compounds of PAHs appear to be random in nature. Other studies suggest a significant role of bacteria, which may contribute to changes in the mobility of bi-directional zinc and lead in the soil depending on the conditions [35]. Since the migration of PAH in a soluble form is small (the concentrations of few ng dm^{-3} of four compounds), the movement of these compounds in the soil should be attributed mainly to the fraction adsorbed on the microparticles, while the metals migrate freely also in soluble forms [28].

A decrease was observed in concentrations of the individual compounds of the experiment after 42 days in comparison to the initial concentration (before pouring). This phenomenon was observed for both tested series. However, for the GP series the recorded concentrations of values were lower by 10.5–89 % compared to the final concentrations recorded for the G series.

Our simulation has not confirmed the increase in PAH concentration achieved in the model experiment in which distilled and sewage water were used to filling [36]. Following the release of water we investigated changes in the occurrence of PAHs in soil. In both cases, until 28th day of the experiment the PAH content increased by 28 and 38 % respectively for distilled and sewage water. After this time there was a decrease in the contents of the tested compounds. However, the behaviour of individual groups of compounds was varied. The strongest growth was recorded for 5- and 6-ring PAH. In the case of the "flood" simulated with distilled water, the final content of PAH (56th day) was less than 11–35 % compared to the start of the experiment. Probably the 7-day flooding by rainwater was too short to initiate the process of formation of PAHs or organic matter content in the soils was too low (3.11 and 3.28 %) for empirical confirmation of this phenomenon, which can occur with low intensity. However, in the case of the use of sewage water in the experiment by Oleszczuk et al, the final concentrations of the test compounds were higher than the initial one, which were from 11 to 130 %. This underlines the negative impact of soil contaminated by floodwaters due to providing substances that can increase the solubility and therefore bioavailability of PAHs [36].

The movement of PAHs along with the water penetrating the soil was tested in similar model experiments. The study was performed on mineral, organic and cultivated soil with organic carbon contents respectively 0.11, 16.3 and 10.1 %. The authors showed significant mobility of PAHs (fluorene, anthracene and pyrene) in mineral soil in which after 20 days of the experiment the tested compounds were recorded at a depth of 36 cm; whereas, in the case of cultivated and organic soil the tested compounds did not exceed the depth of 30 cm after 30 days the experiment. This has to do with the size of sorption complex (especially in the absence of anthropogenic contaminants such as ash or tar) and the permeability of the soils studied [37]. Experiment made here in, and the results obtained, despite the use of light, low in organic matter content soil, have not confirmed so significant motility of test compounds. In the studies the used ash from biomass caused an increase in the levels of certain compounds of PAHs in the layer c on day 14th of the experiment. This was mainly Phe, Flt, Pyr, and 5- and 6-ring PAHs. Then, however, the concentration of PAHs in this layer decreased and on day 42nd of the experiment the highest concentrations of these compounds were recorded in the layer "a" having direct contact with the slit.

Conclusions

The use of prepared silt in a laboratory experiment did not bring the expected results. The expected significant increase of concentration of 16 PAHs in the layer "a" having direct contact with the slit did not occur. A significant increase in the concentrations of PAHs in the soils in the 42nd day of the experiment was observed only in the case of Flt and B[ghi]Per. In the case of acenaphthylene and phenanthrene and pyrene, chrysene, also noted a slight increase in their amount, but only in certain layers of soil cores analysed. The decrease in the sum of the 16 PAHs compounds studied in the 42nd-day experiment, with only periodic increase in the concentrations of individual compounds in the layer c suggests a small degree of transport of these compounds used in the experiment silt in which the content of the analysed compounds was high.

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MIGRACJA WWA W WARSTWIE ORNEJ GLEB ZALANYCH WODAMI POWODZIOWYMI – DOŚWIADCZENIE MODELOWE

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Abstrakt: Gleby okresowo lub stale podmokłe, a także gleby narażone na oddziaływanie wód powodziowych w znacznym stopniu narażone są na zanieczyszczenie związkami nieorganicznymi oraz organicznymi. Są to przede wszystkim te związki, które są nanoszone wraz z napływającą (silnie obciążoną) wodą powodziową, jak i autochtonicznymi wytwarzanymi w obrębie profilu glebowego, na drodze beztlenowych przemian materii organicznej. Związki z grupy WWA są sorbowane przez glebę z wód powodziowych oraz przemieszczają się w profilu glebowym, stanowiąc zagrożenie dla wód podziemnych. Ponadto po ustąpieniu zjawiska powodzi związki te mogą być pobierane przez rośliny uprawne. W pracy badano zanieczyszczenie gleb wielopierścieniowymi węglowodorami aromatycznymi (WWA) pochodzącymi z rozkładu materii organicznej oraz z nanosu powodziowego oraz ich migrację w warstwie ornej gleby.

Słowa kluczowe: powódź, WWA, gleby, migracja zanieczyszczeń

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PHYSICAL FACTORS AFFECTING THE PRODUCTION OF AMYLASE FROM *Bacillus* SPECIES ISOLATED FROM NATURAL ENVIRONMENT

WPŁYW CZYNNIKÓW FIZYCZNYCH NA AKTYWNOŚĆ AMYLOLITYCZNĄ *Bacillus* sp. WYIZOLOWANYCH ZE ŚRODOWISKA NATURALNEGO

Abstract: The influence of different factors on amylolytic activity *Bacillus cereus* (2 strains) and *Bacillus mycoides* (2 strains), isolated from soil samples and water of Turawa Lake has been studied. Effect of physiological (pH of reaction mixture in the range of 4.0–8.0, temperature of reaction from 30 to 60 ^{o}C) and nutritional parameters (the carbon sources and they concentration in medium) were examined spectophotometricaly for their effect on amylase production. The results obtained showed, that in view of all studied factors the least favorable value of pH was 5.0, while in most cases the most favourable for the process of amylase production were following values 7.0 and 8.0. Moreover, it has been stated that the lowest amount of amylase was noted at 30 ^{o}C, and the highest at 60 ^{o}C. In case of amylolytic activity, in view of all temperatures the most effective strain was *B. mycoides* A134 whereas the least *B. mycoides* G3. The best results of amylase production have been achieved for all remaining strains in two cases – on maltose and glucose medium at all tested temperatures. Additionally, soil occurring strains preferred lower concentration of potato starch (*ie* 1 %) when compared with water strains which favoured higher concentration (5 %).

Keywords: *Bacillus cereus*, *Bacillus mycoides*, amylase, physical factors

In recent years intensive studies have been conducted in order to look for new possibilities of environment protection with a view to reducing the chemicals, which contaminate the environment. One of the methods used is the application of biopreparations, bioutilizers based on microbial populations or their enzymes isolated from natural environment – soil, water in the processes of bioremediation, biodegradation, biostimulation and plant protection [1, 2]. Amylases (E.C.3.2.1.0) are an important group of biotechnologically valuable enzymes hydrolysing starch molecules to dextrin, maltose and/or glucose. They are produced by plants, animals and microorganisms, of

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which the last group remains in the centre of attention. Many kinds of bacteria possess the ability to produce the useful enzymes or secondary metabolites, among others bacteria of *Bacillus* spp. [3–5]. They are particularly interesting due to their easy cultivation and high production of extracellular enzymes, high adaptability to adverse environmental conditions and its wide area of potential application. Furthermore, with the advent of new frontiers in biotechnology, the spectrum of the applications of amylase has been widened up to many other fields such as analytical, medicinal and clinical chemistries, as well as their widespread use in the industries such as textile, detergents, paper, food, brewing, pharmaceutical and animal feed [6–11]. According to literature data [6, 10, 12–15] they are varied in terms of their enzymatic activity, that depends on the species of microorganisms and the culturing conditions *eg* pH of the medium, temperature, composition of the growth medium (the source of carbon, nitrogen, phosphate, metal ions and their concentration). Interactions of these parameters are reported to have a significant influence on the productive synthesis of these enzymes. Therefore, they are research being carried out continually, with the purpose of find new, more and more productive strains, able to synthesise a considerable quantity of enzymes. Among the various species of *Bacillus*, *B. licheniformis*, *B. amyloliquefaciens* and *B. subtilis* are used most frequently in the commercial production of amylases [3, 7, 9, 16]. Reference data show that *B. cereus* and *B. mycoides* might be involved in future biotechnological and industrial applications [8, 17]. The purpose of conducted research was to assess the production of amylase by *Bacillus* strains and optimize the parameters for their production.

Materials and methods

The bacterial strains used in this study were *Bacillus* species, previously isolated from soil samples (2 strains marked as *Bacillus cereus* A96 and *Bacillus mycoides* A134) and water of Turawa lake (2 strains marked as *Bacillus cereus* G10 and *Bacillus mycoides* G3).

Determination of amylase production

In the research, *Bacillus* species producing amylase were screened by means of starch hydrolysis procedure followed by a 48 h cultivation at 30°C on modified Waksman medium (consisting of 1.0 g/dm^3 NaCl, K_2HPO_4 1.0 g/dm^3, $(NH_4)_2SO_4$ 2.0 g/dm^3 and $CaCO_3$ 5.0 g/dm^3) [18] with an addition of different carbon source. The effect of potato starch (P), corn starch (C), and maltose (M) at concentrations ranging from 1 % to 5 %, and 1 % glucose (G) was determined, that were added into the basic culture medium. The medium (50 cm^3) was inoculated with *Bacillus* inoculum with an optical density of 2.0 at 560 nm, next incubated at 30 ^{o}C on a rotary shaker at 110 rpm for 48 h. The supernatant of the culture was collected after centrifugation at 4000 rpm for 20 min and subjected to assessment of amylase activity. The amylase activity was estimated on the basis of the reduction in blue color intensity resulting from enzymatic hydrolysis of soluble starch as a substrate following the modified method of Fennala [19] as described previously [20]. Enzymatic activity (U/ cm^3) was examined spectrophotometrically and was defined as the amount of the enzyme which hydrolyzed 1 mg of starch per 1 cm^3 of the extract solution over 30 min of incubation.

Effect of pH and temperature

In order to determine the appropriate pH range of enzyme activity, 0.1M buffers were applied. For pH 5.0 and 6.0 was used citrate buffer, while for pH 7.0 and 8.0 phosphate buffer. In order to evaluate the effect of various temperature on amylase production, the reaction mixtures were incubated at temperatures ranging from 30–60 ^{o}C.

Results and discussion

In the presented paper, 4 bacterial strains of *Bacillus* genus were screened for their ability to synthesize amylolytic enzymes on culture media containing different source of carbon, at pH ranging from 5 to 8 and the temperature ranging from 30 to 60 ^{o}C. In conducted tests, enzymatic activity depended on the medium composition, pH and the temperature, while individual *B. cereus* and *B. mycoides* strains showed varied activity in exocellular amylases production.

In an extracellular amylase biosynthesis the most active strain was *B. cereus* A96 at pH 5.0. The highest amylase amounts were recorded in a maltose growth medium, especially at its highest concentration amounting 5 % (1.58 U/cm^3). Whereas the lowest amylase amounts were noted in case of water occurring strains, of which *B. mycoides* G3 did not produce amylase under the above mentioned pH conditions. None of the strains under study showed enzymatic activity in a glucose medium, similarly to media with 1 % and 2.5 % potato starch and 2.5–5.0 % maltose media (Fig. 1).

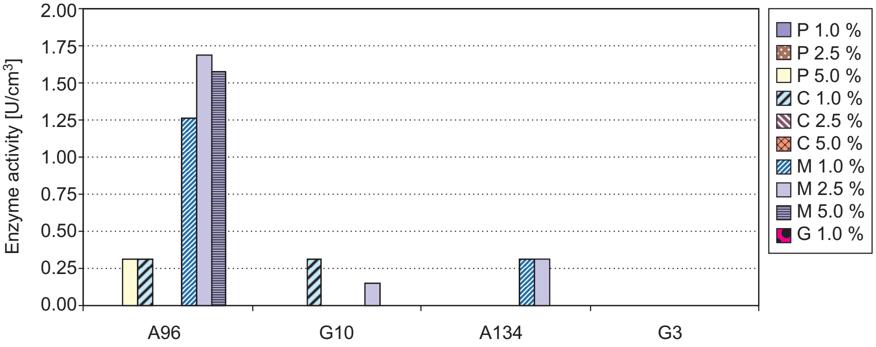

Fig. 1. The influence of pH 5.0 on the production of extracellular amylases by *Bacillus cereus* (A96, G10) and *Bacillus mycoides* (A134, G3)

At consecutive pH value equal to 6.0, it has been displayed that out of all *Bacillus* sp., the water strains demonstrated the highest enzymatic activity, particularly *B. mycoides* marked as G10. The growth medium containing the highest concentration of potato starch (5 %) turned out to be a favourable medium for this strain but at a lower concentration (1 %) for *B. mycoides* G3. Both strains decomposed starch in the amount of 1.22 U/cm^3 and 1.03 U/cm^3 respectively. Whereas in the medium containing corn starch these strains behaved inversely. The lowest amylase activity was found in case of *B. mycoides* A134, nearly 2–4 fold decrease in amylase level was observed in the potato (2.5 %) and the maltose (5 %) media, compared to the other strains (Fig. 2).

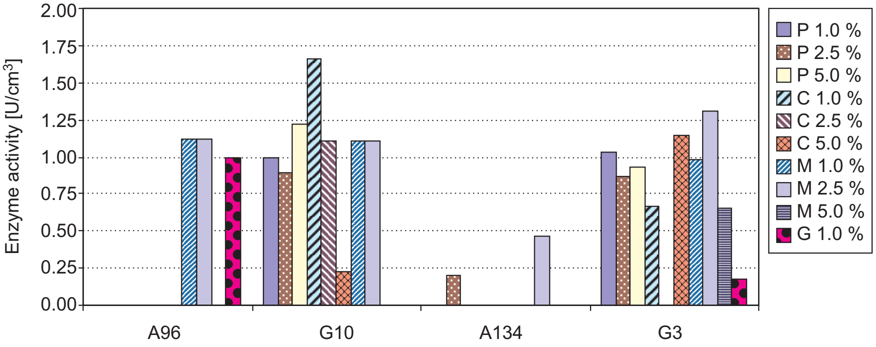

Fig. 2. The influence of pH 6.0 on the production of extracellular amylases by *Bacillus cereus* (A96, G10) and *Bacillus mycoides* (A134, G3)

In contrast to pH 6.0 the maximum production of amylase was noted at pH 7.0 in case of soil occurring bacteria. The most vigorous strain was *B. cereus* A96 in the medium containing corn starch (from 1.24 U/cm^3 to 1.52 U/cm^3), but *B. mycoides* A134 in the potato (2.5 %) and the maltose (1 %) media, 1.25 U/cm^3 and 1.42 U/cm^3, respectively. The growth medium containing lower concentration of potato (1 %) turned out to be favourable for water occurring bacteria (strains G3 and G10) and the quantity of hydrolysed starch amounted to 0.95 U/cm^3 (G10) and 1.01 U/cm^3 (G3). The results related to these carbon sources showed that none of the strains produced enzymes in glucose media, similarly to described results obtained at pH 5.0 (Fig. 3).

Amylase activity measured for *B. cereus* strains and *B. mycoides* strains at pH 8.0 showed, that among the first group of the most active was strain marked A96 while among the second group strain marked G3. Among them, *B. cereus* A 96 preferred the

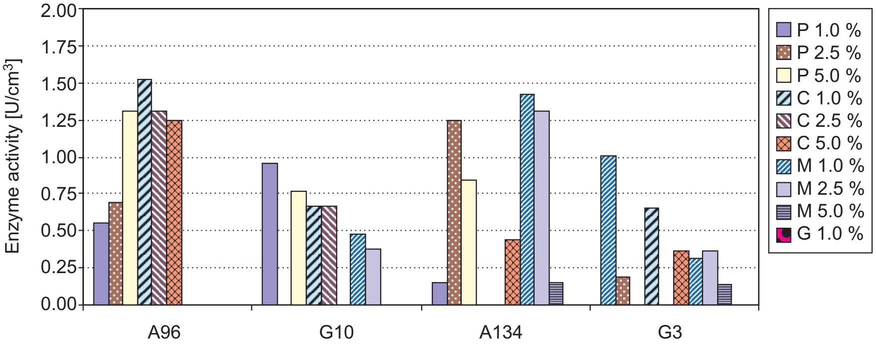

Fig. 3. The influence of pH 7.0 on the production of extracellular amylases by *Bacillus cereus* (A96, G10) and *Bacillus mycoides* (A134, G3)

highest (5 %) concentrations of potato starch, corn starch and maltose, while *B. mycoides* G3 the lowest (1 %). The enzyme activity ranged from 1.18 (P 5 %) to 1.82 (M 5 %) U/cm^3 (A96) and from 0.71 (M 1 %) to 1.50 (P 1 %) U/cm^3 (G3). Moreover, glucose medium was sufficient for amylase production only for *B. cereus* A96 (Fig. 4).

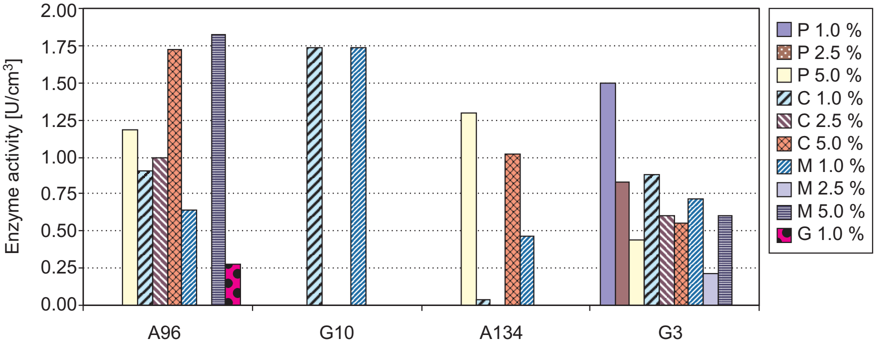

Fig. 4. The influence of pH 8.0 on the production of extracellular amylases by *Bacillus cereus* (A96, G10) and *Bacillus mycoides* (A134, G3)

For further estimation, in order to determine the influence of temperature on productive abilities of *Bacillus* strains, pH 7.0 was selected.

Soil occurring bacteria, both *B. cereus* A96 and *B. mycoides* A134, produced the highest amount of amylase in medium containing 1 % potato starch in a full range of temperature. When *B. cereus* G10 is considered, the highest amounts were noted in P 1 % only at temp. 30 °C and 50 °C while in P 5 % at temp. 40 °C and 60 °C. The lowest amount of amylase were obtained in case of all the strains at 2.5 % concentration of potato starch when compared with all tested temperatures. Besides, among the four tested strains, the most productive were *B. cereus* G10 and *B. mycoides* A 134. The optimal temperature for amylase production occurred to be 60 °C for soil strains and 60 °C or 50 °C for water strains, that they showed the maximum activity (Fig. 5).

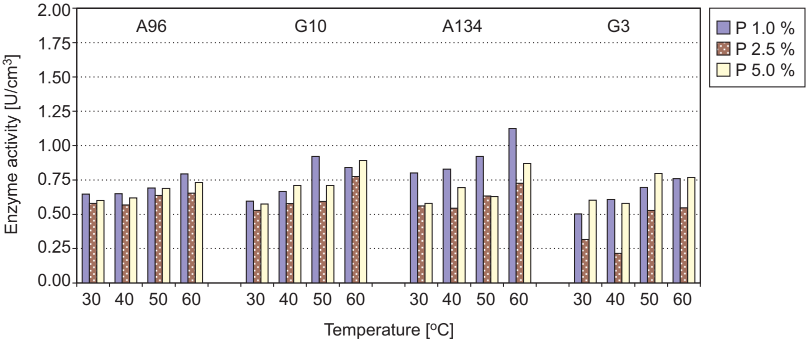

Fig. 5. The influence of temperature on the production of extracellular amylases by *Bacillus cereus* (A96, G10) and *Bacillus mycoides* (A134, G3) grown in potato starch media

Te effect of temperatures and corn starch on amylase production by *Bacillus* strains is presented in Fig. 6.

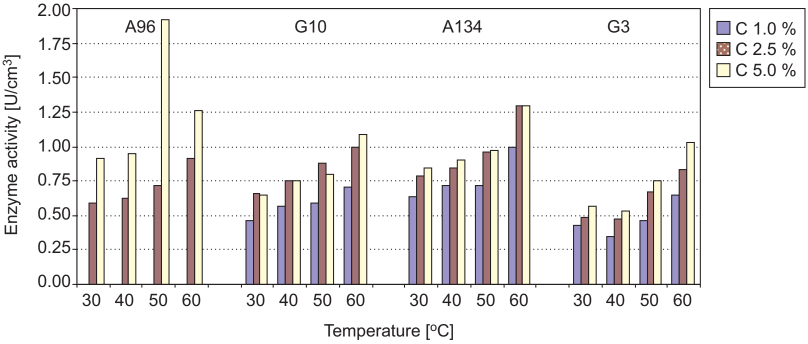

Fig. 6. The influence of temperature on the production of extracellular amylases by *Bacillus cereus* (A96, G10) and *Bacillus mycoides* (A134, G3) grown in corn starch media

The growth medium containing 5 % corn turned out to be a favourable medium for amylase production by all soil occurring strains and one water strain *B. mycoides* G3, while for water strain *B. cereus* G10 they were C 2.5 % and C 5 % media. However, the lowest amylase activity was found in 1 % corn medium for both *B. mycoides* strains and *B. cereus* G10 as well. Only *B. cereus* A96 did not show amylase production at said concentration. It was found that the highest level of amylase was obtained for all strains at 60 ^{o}C and also among *B. mycoides* the highest ability to synthesize amylase was noted for strain marked A 134 (Fig. 6).

The growth medium with maltose appeared to be the most favourable in the biosynthesis process of the amylases compared to all tested media. Based on the obtained results, the highest amount of amylase was observed at 5 % maltose concentration in case of both *B. mycoides* strains and *B. cereus* A96, while at 2.5 % maltose in the event of *B. cereus* G10, in a full temperature range. Maximum amylase production for all strains was obtained at 60 ^{o}C, although *B. cereus* G10 also revealed activity in the remaining temperatures with the results similar to the ones at 60 ^{o}C. Among all strains, *B. cereus* G10 and *B. mycoides* A134 presented the highest enzymatic ability (Fig. 7).

The last medium, with 1 % glucose, was promoting extracellular amylase production. The highest amount of amylase in this medium was obtained at 30 ^{o}C in case of both *B. mycoides* strains, but the lowest amounts were recorded at higher temperatures (50 ^{o}C for A134 and 60 ^{o}C for G3). A different situation appeared in case of *B. cereus* strains. The highest activity was observed at 40 ^{o}C for strain marked A96 and at 60 ^{o}C for G10, whereas the lowest at 50 ^{o}C for the both strains. The quantity of hydrolysed starch fluctuated around 1.95 U/cm^3 in case of all strains (Fig. 8).

A number of reports available in the literature indicate that the biosynthesis of various extracellular enzymes or secondary metabolites depends on many external factors such as the type and concentration of the substrate, the presence of easily

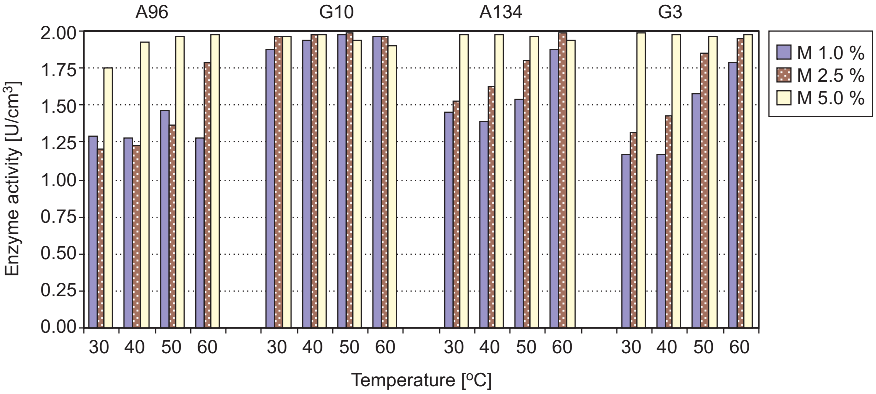

Fig. 7. The influence of temperature on the production of extracellular amylases by *Bacillus cereus* (A96, G10) and *Bacillus mycoides* (A134, G3) grown in maltose media

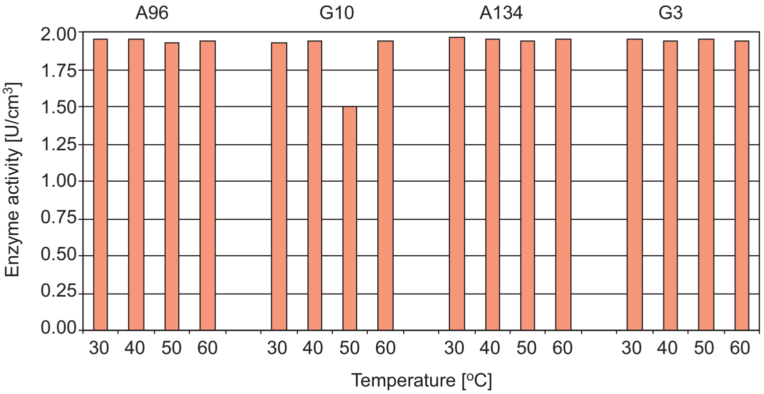

Fig. 8. The influence of temperature on the production of extracellular amylases by *Bacillus cereus* (A96, G10) and *Bacillus mycoides* (A134, G3) grown in glucose (1 %) medium

available sources of carbon and enzyme activator, pH, the temperature but also on the genus and even the strain of microorganisms Earlier studies of many researchers reported that amylases are active in a wide range of pH 5–11 and temperatures between 30–80, although their study have shown different optimal conditions for amylase activity depending on *Bacillus* strains [3, 21–24]. Annamalai et al [17] have shown that the optimal pH of amylase activity for *B. cereus* ranged between 8–11. In contrast to the present study, *B. cereus* MTCC 1305 revealed amylase at pH 5.0 [8] but in another *B. cereus* strain maximum amylase production was observed at pH 7.0–8.0 [12]. Slightly different results have been obtained in our study. In most cases, the most suitable pH was 7.0, though *B. mycoides* G3 and *B. cereus* G10 showed also high activity at pH 6.0 (Fig. 2, 3). Additionally, the highest activity of almost all strains under study have been noted at 60 °C, although amylases proved to be active in slightly lower temperatures ranging from 30 to 60 °C. Similarly, the following results for amylase activity have been reported by others in case of: *B. cereus* – 55–65 °C [8, 17], *B. megaterium* – 60 °C [25] and higher in case of: *B. amyloliquefaciens* 40 °C [26] and *Bacillus sp.* 35 °C [5], *B. cereus* 30 °C [24] or 40 °C [12]. Studies Deb et al [27] revealed that optimum pH, temperature of enzyme activity of *B. amyloliquefaciens* was 6,5 and 60 °C respectively. Other investigator reported that maximum amylase production occurred at pH 6.0 and temperature 37 °C [28]. Viswanathan et al [29] has evaluated the amylolytic activity of three strains *of Bacillus*, such as *B. subtilis, B. cereus* and *B. megaterium* and showed that this latter was found to the best amylase producer. Maximum enzyme production was observed in pH 7.0 and temperature 37 °C.

Among the carbon sources tested, 5 % maltose and 1 % glucose have been found to enhance amylase production. Lower levels of amylase have been noted in potato medium (Fig. 7, 8). On the other hand Sivakumar et al [12] observed the maximum amylase production in maltose supplemented medium while minimum amylase production in glucose medium. Other studies [30] indicate sucrose as the best carbon source to enhance amylase production by *B. cereus* strain A 26MB. In view of all temperatures the most effective was *B. mycoides* A 134 whereas the least *B. mycoides* G3.

Many researches [8, 13, 21] concluded that the synthesis of amylase was greatly suppressed when the bacteria were grown on sucrose, glucose or fructose and amylase production whereas enhanced when the bacteria were grown on starch. Izviekova, 2005 and Saxena et al, 2007 showed that in the media rich in available monomers, the bacteria absorb these components, whereas in poor media they produce hydrolytic enzymes to degrade complex molecular substrates. In contrast, there are reports indicating stimulating effect of monosaccharides or disaccharides on amylase production. Anto et al, 2006 and Jamuna et al, 1992 observed that amylase production by *B. cereus* MTCC1305 and *B. subtilis* respectively were higher in the medium with glucose than with potato. Viswanathan et al [29] tested diverse carbon source such as sucrose, starch, glucose and maltose, high production was recorded with starch followed by glucose while the least production of enzyme was noted when sucrose was used as a carbon source.

The selection of an appropriate the culture conditions to determine the metabolic process, as well as the substrate is very important because it enables to find the most active strains useful for the production of biological preparations, which can be used in protecting the environment as well as a useful alternative to chemical methods.

Conclusions

The research proved significant diversity of amylolytic activity of *B. cereus* and *B. mycoides* strains, towards the source of carbon substrates, pH and the temperature analysed in the experiment. Biosynthesis of amylase catalyzed by *Bacillus spp.* at different pH was most varied and depended on the strain and the growth medium. The least favourable pH was 5.0 while in most cases the best noted pH was 7.0. The research enables to state that all tested bacteria hydrolysed starch and the process was intensive for *B. mycoides* G3 at pH 8.0 and *B. cereus* G10 at pH 6.0. Taking into account temperatures range tested, the highest amount of amylase was obtained at 60 °C while the lowest at 30 ^{o}C for all tested strains. Simultaneously, the growth medium with an addition of 5 % maltose and 1 % glucose was most suitable for all tested strains. Considering the temperature and sources of carbon, the most effective strain was *B. mycoides* A 134 whereas the least *B. mycoides* G3.

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WPŁYW CZYNNIKÓW FIZYCZNYCH NA AKTYWNOŚĆ AMYLOLITYCZNĄ *Bacillus* sp. WYIZOLOWANYCH ZE ŚRODOWISKA NATURALNEGO

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Abstrakt: Celem badań była ocena wpływu różnych czynników na aktywność amylolityczną *Bacillus cereus* (2 szczepy) i *Bacillus mycoides* (2 szczepy) wyizolowanych z gleby i Jeziora Turawskiego. Metodą spektrofotometryczną badano wpływ pH mieszaniny reakcyjnej w zakresie od 5.0 do 8.0 i temperatury w zakresie od 30 °C do 60 °C oraz źródła węgla i jego koncentracji w podłożu na poziom produkowanych amylaz. Stwierdzono, iż najgorszą wartością pH do syntezy amylaz było 5.0, natomiast najlepszą, w większości przypadków pH 7.0. Uwzględniając zakres badanych temperatur, najwyższą aktywność uzyskano w temp. 60 °C, natomiast najniższą w temp. 30 °C dla wszystkich testowanych szczepów. Najbardziej aktywnym szczepem był *B. mycoides* A 134, natomiast najmniej *B. mycoides* G3.

Słowa kluczowe: *Bacillus cereus*, *Bacillus mycoides*, amylazy, czynniki fizyczne

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NITRATES CONCENTRATION IN PERCOLATING WATER IN RELATION TO DIFFERENT TYPES OF FERTLIZATION IN MOUNTAIN MEADOW

ZAWARTOŚĆ AZOTANÓW W WODZIE PRZESIĄKOWEJ W ZALEŻNOŚCI OD RODZAJU NAWOŻENIA ŁĄKI GÓRSKIEJ

Abstract: Specificity of highland agriculture is high contribution of natural fertilizers in feeding farm lands. This manner of fertilisation had been evaluated in terms of crop production effect. However, an evaluation of its influence on water environment was missing. This is the reason why the authors decided to assess an effect of folding on nitrogen content in water passing through the soil horizon of a highland meadow and NO_3-N loads leached away. The study took place in 2007–2009 in the mountain grassland by the type of red fescue and common bent-grass. Experimental objects involved a control and four fertilization treatments *eg* one with inorganic fertilizers, and three with manure from sheep folding. Each type of fertilization significantly changed the floristic composition of the sward. These changes increased the outflow of water from the soil profile. Inorganic nitrogen fertilization proved to be more safe for water environment, when set beside folding. Gross NO_3-N loads leached out by water for the whole experimental period amounted to 15–21 % share of nitrogen fertilization input for the folding objects, and 6 % for the inorganic fertilization one. Exceptionally heavy load left the high-density fold in the first year after treatment. This reached as much as 81 % of gross load for 3-year experimental period.

Keywords: mountain grassland, folding, percolation water, nitrates, losses

Introduction

Among all of major nutrients nitrogen is the one noted for greatest losses. They are caused by its remarkable ability to volatilize to the atmosphere and to be leached away from the soil. Amount of such loss depends on the level and type of fertilization as well as on the intensity of organic matter mineralization process in soil [1, 2]. On the basis of calculations done by Sapek [3] it is known that every year from the whole area of Poland about 1800 tons of this nutrient is transported by rivers to the Baltic Sea, while

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agriculture input to the whole nitrogen load is estimated at a rate of about 70 %. Chemical properties both of stream water and underground water are strongly influenced by a status of farming economy in highland regions, which are concerned to be a place, where water resources develop. Specificity of highland agriculture is high contribution of natural fertilizers in feeding farm lands, including fresh manure, and excreta of folded sheep in particular. This manner of fertilization had been evaluated in terms of its influence on crop production by several researchers [4–6]. However, there is no similar evaluation for its possible effect on water environment. This is the reason why the authors decided to assess an effect of folding on nitrogen content and load of NO_3-N leaving a mountain meadow with water passing through the soil horizon.

Material and methods

The study took place at Czarny Potok near Krynica (N 49°24′57″, E 20°55′32″) in a mountain meadow (640 m a.s.l.) by the type of red fescue (*Festuca rubra*) and common bent-grass (*Agrostis capillaris*) in years 2007 to 2009. The soil over an experimental field was brown, classified with texture as weak loamy sand, with acid reaction ($pH_{KCl} = 4.3$). The soil was fairly rich in potassium (70 $mgK \cdot kg^{-1}$), however very poor in phosphorus (8.0 $mgP \cdot kg^{-1}$ soil). In order to determine plant effect on changes of NO_3-N content in soil a yearly research cycle was divided into two periods: summer (15 April to 15 October) and winter one (16 October to 14 April). Experimental objects included control and four fertilization treatments *eg* one with inorganic fertilizers, two manured by folded sheep and one fold-manured along with yearly application of inorganic nitrogen and phosphorus (10 $kgP \cdot ha^{-1}$ and 50 $kgN \cdot ha^{-1}$). Sheep folding was performed in spring 2007. The two folding objects were differentiated according to stock density into a low-density fold and a high-density fold. In the former case an area assigned for 2 nights per 1 sheep was of 2 m^2, while in the latter it was 1 m^2. As regards the inorganic fertilization object minerals were applied yearly: phosphorus and potassium as a single dose in spring, while nitrogen dose was divided in two parts, 60 % in spring and 40 % for 2nd regrowth. Every year the meadow was mowed twice. First cut at the beginning of the flowering stage and the second after approximately 8 weeks. The surface area of a field object was 50 m^2. Each object was fitted with 3 lysimeters dug into the ground at a 40 cm depth, because of soil horizon structure. Water from lysimeters was conveyed through hosepipes to plastic containers. The amounts of oozing water were measured several times as it appeared there, and samples containing 10 % of its volume were taken for chemical analysis. All specimens from each experimental period were collected together to make up a total sample; they were stored in a refrigerator. These total samples were subject to the estimation of NO_3-N content using microprocessor-controlled photometer LF205. As far as amount of precipitation is concerned, it was measured with a Hellman pluviometer placed in the experimental field. Nitrate nitrogen loads were calculated by multiplying nitrogen content by an amount of percolated water. Because of the changes that have occurred in the botanical composition of the sward, in the 2nd year of research its assessment was performed by Klapp's technique. Obtained data on amounts of percolated water and

NO_3-N loads leaving the soil underwent the analysis of variance, and mean values compared with the use of Student's t-test.

Results

Sward of control object was dominated by two species of grasses (Table 1).

Table 1

Floristic composition of mountain meadow sward (1st regrowth) in the 2nd year of the study [%]

Species	Fertilization				
	Control – 0	Inorganic $P_{25}K_{50}N_{120}$	Fold		
			Low density $P_{14}K_{147}N_{92}$	Low density + $P_{10}N_{50}$	High density $P_{28}K_{294}N_{184}$
Festuca rubra	28	15	19	13	14
Agrostis capillaris	23	9	12	8	6
Anthoxanthum odoratum	9	2	5	2	2
Festuca pratensis	5	24	15	22	25
Poa pratensis	3	12	8	10	10
Dactylis glomerata	+	5	2	2	3
Elytrigia repens	+	5	2	2	2
Phleum pratense	—	+	3	5	5
Trifolium repens	6	3	12	8	6
Plantago lanceolata	6	2	3	1	1
Taraxacum officinale	1	5	3	3	6
Rumex acetosa	+	3	1	3	4
Ranunculus repens	+	3	3	3	4
Others	17	12	12	18	12

+ – less than 0.5 %.

These dominated species were red fescue (*Festuca rubra* L.) and common bent grass (*Agrostis capillaris* L.) constituting more than 50 % yield of the sward. Next to them in smaller amounts were still sweet vernal grass (*Anthoxanthum odoratum* L.), meadow fescue (*Festuca pratensis* Huds.) and smooth-stalked bluegrass (*Poa pratensis* L.). White clover (*Trifolium repens* L.) was present in an amount of 6 % yield, and other dicotyledonous completed floristic composition – in largest amount occurred plantain (*Plantago lanceolata* L.) – 6 %.

Each type of fertilization negatively affected the number of species that dominated the control sward. The share of red fescue in the object of loose fold decreased by 1/3 and twice in case of other objects. At the same time, the loss of common bent grass in these objects was 2-fold and 3–4-fold, respectively. In contrast, species that have spread in large quantities under the influence of fertilization were among grasses meadow fescue and Kentucky bluegrass, and smaller quantities of orchard grass (*Dactylis* *glomerata* L.), quack grass (*Elytrigia repens* L.) and timothy (*Phleum pratense* L.). Among the dicotyledonous plants biggest gain in yield was found in the common dandelion (*Taraxacum officinale* L.), sorrel (*Rumex acetosa* L.) and buttercup (*Ranunculus repens* L).

The highest precipitation totals for vegetative seasons were characteristic of year 2007, and the lowest one of 2009 (Table 2).

Table 2

Total precipitation and amounts of water passing through soil horizon

Type of fertilization	Summer period			Winter period	
	2007	2008	2009	2007/2008	2008/2009
	Total precipitation [mm]				
	732	664	619	431	468
	Amount of water soaking through soil horizon [mm]				
Control – 0	170	190	62	346	280
Inorganic $P_{25}K_{50}N_{120}$	217	258	177	350	282
Low-density fold $P_{14}K_{147}N_{92}$	177	186	165	351	297
Low-density fold + $P_{10}N_{50}$	185	232	179	346	292
High-density fold $P_{28}K_{294}N_{184}$	213	212	190	356	294
$LSD_{\alpha = 0.05}$	18	26	22	40	33

The difference in whole summer rainfall between these years equals 113 mm. Precipitation totals for winter periods were similar to each other and evidently lower to those for vegetative seasons. Any summer period had a share of about 60 % of yearly precipitation. The greatest amounts of water passing through a soil horizon in a vegetative season were noted for 2008 while the least in 2009, which was characterized by less rain. In this year water outflow coefficients (the ratios of percolating water outflow to precipitation inflow) ranged from 28 % to 39 %, while in the other years they were found either 23–30 % or 10–31 %. As regards winter periods water outflow coefficients were significantly higher when compared to those in summer periods. They amounted to about 81 % for the first winter period, and 62 % for the second one, being similar among objects. With regard to summer periods the lowest water outflow coefficients were characteristic of the control object (average water outflow coefficient for the period of study was approximately 20 %), while the highest ones were noted for both inorganic fertilization and high-density folding object, where their values were half as great as the control.

For each experimental period percolating water from the control object had the lowest NO_3-N concentration (Table 3). This water was 2–7 times poorer in nitrates than water from the object fertilized with minerals alone.

Table 3

NO_3-N levels in percolated water [$mg \cdot dm^{-3}$]

Type of fertilization	Summer period			Winter period	
	2007	2008	2009	2007/2008	2008/2009
Control – 0	0.96	0.53	0.32	0.30	0.38
Inorganic $P_{25}K_{50}N_{120}$	2.19	1.41	1.16	2.27	1.07
Low-density fold $P_{14}K_{147}N_{92}$	3.09	0.74	0.61	1.56	0.60
Low-density fold + $P_{10}N_{50}$	5.72	1.72	1.25	4.98	0.67
High-density fold $P_{28}K_{294}N_{184}$	5.92	1.30	1.04	5.22	0.88

In the first year after spring folding seepage water from each folded object contained high amounts of such nitrogen form, both in vegetative and winter periods. For the high-density fold and the low-density one supplied with minerals their NO_3-N levels were 2.5 times higher than in the case of inorganic fertilization object. In the succeeding years water from them had similar NO_3-N content as the inorganic fertilization object. As regards water from the low-density fold, it contained 2 times less of NO_3-N than those two, although this measure was twice as much as in the control.

Loads of NO_3-N leached out by percolating water are shown in Table 4.

Table 4

NO_3-N loads transported by percolating water [$kg \cdot ha^{-1}$]

Treatment	Summer period			Winter period		Total
	2007	2008	2009	2007/08	2008/09	
Control – 0	1.63	1.01	1.98	1.04	1.06	6.72
Inorganic $P_{25}K_{50}N_{120}$	4.75	3.64	2.05	7.94	3.02	21.40
Low-density fold $P_{14}K_{147}N_{92}$	5.47	1.38	1.01	5.48	1.78	15.12
Low-density fold + $P_{10}N_{50}$	10.58	3.99	2.24	17.23	1.96	36.00
High-density fold $P_{28}K_{294}N_{184}$	12.61	2.76	1.98	18.58	2.59	38.52
$LSD_{\alpha = 0.05}$	1.20	0.41	0.29	1.40	0.32	3.62

For the whole experimental period such value amounted to 6.71 $kg \cdot ha^{-1}$ from the control, which was more than 3-fold lower when compared to the inorganic one, and as much as 6 times lower than for low-density fold combined with minerals and high density fold. Especially high loads were transported from these two objects in the first year after folding. Their respective shares in gross loads leached out during the study were 77 % and 81 %, whereas for winter period alone this portion amounted to 48% in both objects. It is worth noting that in the two periods of the winter elevated load of NO_3-N in the fertilized objects ranged from 48 % to 55 % of the total load, which was greater than the total load in the three summer periods, which amounted to 45–52 %.

Discussion

Great soil water outflow in winter periods was due to lack of water uptake by plants and reduced evaporation from soil. However, a considerable difference observed between both the analyzed winter periods despite similar levels of precipitation must be attributed to different degrees of soil freezing decisive for the amount of percolated liquid. In the winter period 2008/2009 mean temperature was by 1 ^{o}C lower when compared to the 2007/2008 one, nevertheless for January and February temperature in 2009 occurred to be even 3–4 times lower. This was the reason for more intense freezing of the soil, then reduced percolation of water, while surface runoff was greater, especially due to water from melting. On the other hand the differences in the amount of percolating water between the objects should be combined with the floristic composition of the sward. The control object, characterized by the smallest amount of water that outflow from the soil profile, was dominated by species forming very good sod – with whom is positively related water retention. However, in other objects the loss of these species in favour of others, forming rather loose turf, was the cause of the movement of large quantities of water through the soil profile. This is confirmed, among others by Merz et al [7] and Sulas et al [8]. From the data reported by Sapek [9] it appeared that the origin of nitrogen leached out of the soil by percolating water is not only in fertilization, but also in mineralization of organic matter, and the latter process is stimulated by fertilizers. According to that author the amount of nitrogen released from the soil due to mineralization of organic matter on mineral soils richer in organic matter without plant cover reaches up to 430 kgN $\cdot$ ha^{-1} $\cdot$ y^{-1}. This supposition may explain the elevated levels of NO_3-N in percolated water found for the inorganic object in the first year after treatment, where the soil had been accumulated certain amount of organic matter prior to fertilization.

High concentration of NO_3-N in percolating water as well as immense nitrogen loads leached from the soil of folded objects for both periods in the first experimental year would cause some trouble, because folding is considered as environmentally friendly manner of fertilization. In fact, first-year leached nitrogen, as NO_3-N alone, amounted to 20 % of total nitrogen delivered by fertilization for both the high-density fold and the low-density fold supplied with minerals. As regards the inorganic fertilization object the respective proportion was almost half the size of the previous one. The amounts of NO_3-N transported out of the soil by seeping water stay within the limits specified by Sapek [11]. In her opinion this kind of loss depends on various factors (nitrogen dose, type of fertilizer, time of application, site conditions) and may vary from 5 to 20 % of nitrogen supplied by fertilization. The reason why the first-year nitrogen loss for each folded object was so heavy is, apart from the ample supply of easily leachable nitrogen from urine, because sheep, especially the dense-fold ones, caused a lot of damage to the turf, which in turn encouraged nitrogen escape. Remarkable nitrogen loss during the first year after folding must be ascribed to its relatively low efficiency rate of uptake from natural fertilizers. According to Mazur [11] the rate of nitrogen uptake from barnyard manure reaches approximately 50 %.

Significant nitrogen loss due to the surface-spreading of natural fertilizers can be assumed given the results reported by Svensson [12]. As the author stated, to postpone ploughing land-spread manure for 4 hours instead of performing it immediately would increase nitrogen loss even 6 times.

Conclusions

Based on the experimental data we came to the following conclusions:

1. Each type of fertilization clearly changed the floristic composition of meadow sward, leading to loosening of sod and a larger outflow of water from the soil profile.

2. In winter periods coefficients of water outflow from a soil horizon were 2–3 times higher than in summer ones. Moreover, in winter periods neither a type of fertilization nor its level affected the volume of water leaving the soil horizon. As regards summer periods the lowest amounts of water soaked through the control object, while the highest through the objects with intensive fertilization.

3. Fertilization by means of folding, with the high-density fold or the low-density fold supplied with inorganic fertilizers was a source of significant nitrate-nitrogen loads entering water environment, particularly in the first year after treatment. The amount of NO_3-N leached out of those folds made almost 20 % of nitrogen delivered in fertilizers, in contrast to the inorganic fertilization, where it was 10 %.

4. Because of easy leaching NO_3-N out of the soil in fertilization of mountain grasslands by means of folding one should use a low-density fold. This way of fertilization need to be repeated every 2–3 years depending on sheep stocking rate and alternated with inorganic fertilization.

5. Feeding with inorganic nitrogen, when compared with folding, occurred to be more safe for water environment. Gross N-NO_3 loads leached out for the whole experimental period amounted to 15–21 % of nitrogen delivered from fertilization for the folding objects and 6 % for the inorganic fertilization one.

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ZAWARTOŚĆ AZOTANÓW W WODZIE PRZESIĄKOWEJ W ZALEŻNOŚCI OD RODZAJU NAWOŻENIA ŁĄKI GÓRSKIEJ

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Abstrakt: Celem badań była ocena wpływu nawożenia łąki górskiej z wykorzystaniem koszaru przy udziale owiec na zawartość azotanów (N-NO$_3$) w wodzie przemieszczającej się przez profil glebowy. Badania przeprowadzono w latach 2007–2009. Uwzględniono w nich 5 obiektów: kontrolę i 4 obiekty nawożone. Jeden z tych obiektów był nawożony wyłącznie nawozami mineralnymi ($P_{25}K_{50}N_{120}$), dwa obiekty nawożono tylko przez koszarzenie (koszar luźny $P_{14}K_{147}N_{92}$ i koszar ciasny $P_{28}K_{294}N_{184}$), jeden obiekt obejmował nawożenie kombinowane, w którym koszar luźny uzupełniono nawożeniem mineralnym ($P_{10}N_{50}$).

Koszarzenie przeprowadzono wiosną 2007 r., a przed jego wykonaniem wyceniono skład florystyczny runi. W przypadku koszaru luźnego przez okres 2 nocy dla jednej owcy przydzielono 2 m^2 powierzchni pastwiska, a w koszarze ciasnym 1 m^2. W obiektach z nawożeniem mineralnym nawozy stosowano corocznie. Na każdym obiekcie o powierzchni 50 m^2 były wkopane po 3 lizymetry głębokość 40 cm (z racji takiej miąższości gleby) celem określenia ilości wody przesiąkowej. Łąkę koszono 2 razy w roku. Ilość wody przesiąkającej przez profil glebowy mierzono w miarę jej pojawienia się w odbieralnikach, zaś ilość opadów atmosferycznych mierzono wykorzystując deszczomierz Hellmana.

Każdy rodzaj nawożenia wyraźnie zmienił skład florystyczny runi łąkowej, doprowadzając do rozluźnienia darni i większego odpływu wody z profilu glebowego. Nawożenie z wykorzystaniem koszaru ciasnego lub luźnego w połączeniu z nawozami mineralnymi, zwłaszcza w pierwszym roku po zastosowaniu, było zabiegiem istotnie obciążającym środowisko wodne azotem azotanowym. Ładunek N-NO$_3$ wynoszony z gleby w tych obiektach stanowił prawie 20 % ilości azotu dostarczonego w nawozach, wobec 10 % ilości tego składnika traconego w obiekcie nawożonym nawozami mineralnymi. Do nawożenia górskich użytków zielonych metodą koszarzenia z racji podatności na wymywanie N-NO$_3$ z gleby należy stosować koszar luźny. Nawożenie azotem mineralnym w porównaniu z koszarzeniem okazało się bezpieczniejsze dla środowiska wodnego. Za cały okres badawczy z obiektów koszarzonych ładunek N-NO$_3$ wyniesiony z wodą stanowił 15–21 % ilości azotu dostarczonego w nawożeniu wobec 6 % w przypadku stosowania azotu mineralnego.

Słowa kluczowe: łąka górska, koszarzenie, wody przesiąkająca, azotany, straty

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ASSESSMENT OF DEGREE OF TRACE ELEMENT POLLUTION OF SOIL AND ROOT VEGETABLES

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Abstract: The investigations were focused on determining the level of trace element pollution of soil and root vegetables cultivated for human consumption in the Miechowski county. The collected soils differed in view of their floatable particles, colloidal clay and organic matter content, as well as pH value. Differences in the total content of trace elements and the content of their soluble forms extracted with 0.1 mol · dm^{-3} HCl solution also occurred.

The total content of trace elements in the analysed soils and their soluble forms were determined by soil reaction. Geometric mean of total heavy metals content in the studied soils was as follows: 55.08 mg Zn · kg^{-1}, 8.08 mg Cu · kg^{-1}, 10.05 mg Ni · kg^{-1}, 19.85 mg Pb · kg^{-1} and 0.46 mg Cd · kg^{-1}. The assessment of heavy metals content in the analysed soils was conducted according to the framework guidelines for agriculture elaborated by IUNG. In this respect 44 of analysed samples were classified as soils with natural heavy metals contents. The content of trace elements in cultivated root vegetables was determined by the species, analysed plant part and soil pH.

The content of these elements was much higher in plant tops than in roots. For instance, if one assumes geometric mean of cadmium and lead content in parsley roots grown in soil with pH ≤ 6.5 as 100, cadmium concentration in leaves was higher by 64 %, and lead content was higher by 36 %. On the basis of the obtained results, content of trace elements in vegetable roots was assessed assuming the critical levels of trace element in agricultural products stated by IUNG. Taking into consideration these criteria was stated that all samples of the vegetable roots fulfilled the requirements of usefulness for human consumption in respect of copper and nickel contents, and majority of them in respect of lead content. However, 7.6 % of samples did not fulfil these requirements because of excessive content of lead (> 1 mg · kg^{-1}), 52.5 % of zinc (> 50 mg · kg^{-1}), and as much as 81.6 % samples because of cadmium excess (> 0.15 mg · kg^{-1}), despite their being cultivated in majority in soils with natural these metals content. Excessive content of copper and nickel was registered only in 1.3 % of tops samples, lead in 51.3 %, zinc in 79.7 %, and cadmium in 98.1 % of tops samples, in which 7.6 % of tops samples did not meet fodder requirements for zinc, and as much as 65.8 % for cadmium.

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Taking in to account all roots and tops samples, only 0.6 % of them did not meet criteria of usefulness for human consumption, because of copper and nickel excess, 29.4 % for lead, 66.1 % for zinc, and as much as 89.9 % of samples contained excessive amount of cadmium. Moreover, in 3.8 % of samples Zn content exceeded admissible values in fodder and in 32.9 % contained excessive amount of Cd.

Keywords: soil, root vegetables, content of Cu, Zn, Cd, Pb and Ni

Introduction

A characteristic feature of heavy metals is their considerable ability to accumulate in soil and plants. An increase in the content of these metals in the soil-plant system poses a hazard to animals and people. Exceeding critical element content in soil has an inhibitory effect on plant growth, leading to changes in plant chemical composition [1–3]. Total contents of individual heavy metals in the soils of Poland fluctuate widely: from 0.01 $mg \cdot kg^{-1}$ to over a dozen, reaching even several hundred $mg \cdot kg^{-1}$, depending on many factors [1]. Investigations conducted by numerous authors revealed that heavy metal uptake by plants depends on: the forms and concentrations of individual metals in the substratum, pH value, species and variety of plants, kind of applied organic and mineral fertilizers, etc. [2–5]. These factors may decide about a stimulating or limiting effect on the uptake of these metals by plants. Therefore, some agrotechnical measures aim to reduce heavy metal availability in the soil-plant system [3, 6, 7]. The content of trace metals (zinc, copper, nickel, lead, cadmium) is usually determined in crops cultivated for human consumption, animal feed or industrial use.

The presented research aimed to determine the usefulness for human consumption of root vegetables cultivated in the soils with natural content of heavy metals (zinc, copper, nickel, lead, and cadmium).

Materials and methods

In the first decade of September 2003, 44 soil samples were collected from the depth of 0–25 cm of arable land topsoil from the Miechowski county. Each of the analysed soil samples was an average of between 10 and 20 individual samples (0.5–1.0 kg of soil). The places of sample collection were described in the “Material and methods” section in the first part of the paper [8]. Basic physical and chemical properties of soils were determined in air-dried samples by means of methods commonly used in agrochemical studies: granulometric composition by Bouyoucose-Casagrande aerometric method in Proszynski’ modification, pH by potentiometer in soil suspension in H_2O and in 1 $mol \cdot dm^{-3}$ KCl solution (1:2.5), hydrolytic acidity by Kappen’s method, and organic carbon content by Tiurin’s method [9].

The total content of trace elements in the analysed soils was assessed after previous mineralisation at 450 ^{o}C. Subsequently, the samples were digested in a mixture of perchloric and nitric acids (2:3, *v*/*v*) and dissolved in HCl [9]. Concentrations of trace element soluble forms were assessed in 0.1 $mol \cdot dm^{-3}$ HCl solution. Vegetables (red beetroot, carrot, parsley and celery) at full consumption maturity were taken from the same places as the soil samples. Analysed plant sample was an average of 12 samples (about 1 kg of fresh mass). The plant material prepared for analyses was dry-mineralised. The obtained ashes were dissolved in nitric acid diluted with water at 1:2 (*v*/*v*) ratio to obtain the solutions in which trace element concentrations were assessed by means of ICP AES method. The obtained results were used to compute simple correlation coefficients (r) between the content of trace elements in soils and selected physico-chemical soil properties.

Results and discussion

Contents of trace elements in soil. The soil samples gathered in the Miechowski county varied according to their physico-chemical properties. The pH value of the analysed soils assessed in water suspension ranged from 5.14 to 7.64, and from 4.13 to 7.23 when measured in 1 mol · dm^{-3} KCl solution. The organic carbon content ranged from 6.8 to 16.1 g · kg^{-1}, at geometric mean 10.1 g · kg^{-1}, whereas the content of floatable particles fluctuated from 25 to 52 %, and the content of colloidal clay was from 1 to 23 %. The site of soil and plant samples collection as well as some physico-chemical properties of soils were presented in the first part of this paper in the "Materials and methods" section [8].

Total contents of trace elements in the analysed soils and the content of their soluble forms assessed in 0.1 mol · dm^{-3} HCl solution were diversified (Table 1). Taking in to consideration texture of studied soils one may recognize as natural content of Pb, Cu and Ni and natural to increased content of Zn and Cd [9].

Table 1

Statistical parameters of trace elements concentration in soils

Parameter	Zn	Cu	Ni	Pb	Cd
Total content [mg · kg^{-1} d.m.]					
Minimum	34.5	4.64	5.94	14.80	0.23
Maximum	93.25	11.48	16.08	31.80	0.86
Arithmetic mean	56.02	8.21	10.24	20.40	0.49
Geometric mean	55.08	8.08	10.05	19.85	0.46
Standard deviation (SD)	12.04	1.40	1.95	4.81	0.14
Relative standard deviation (RSD) [%]	21.41	17.99	19.06	23.58	29.77
Content of soluble forms [mg · kg^{-1} d.m.]					
Minimum	0.87	0.14	0.12	0.09	0.07
Maximum	28.9	2.58	3.21	11.15	0.73
Arithmetic mean	16.20	1.49	1.15	4.78	0.39
Geometric mean	13.13	1.16	0.82	2.52	0.36
Standard deviation (SD)	7.58	0.73	0.66	3.24	0.17
Relative standard deviation (RSD) [%]	46.79	49.12	57.74	67.68	42.36

The share of the content of soluble forms assessed in 0.1 mol · dm^{-3} HCl solution in the total heavy metal content fluctuated widely depending on the analysed element, *eg* for copper it was on the level of 14 %, for cadmium it was on the level of 78 %. The content of trace elements in soil, and therefore their bioavailability, is determined by many factors: the bedrock, soil forming processes, pH value, and anthropogenic factors [1, 6]. In the analysed soils, the pH value determined the content of metal soluble forms (Table 2).

Table 2

Parameter of trace elements concentration in soils [mg · kg^{-1}] depending on soil pH value

Parameter	Total content				
	Zn	Cu	Ni	Pb	Cd
pH in 1 mol KCl · dm^{-3} ≤ 6.5					
Range	47.75–93.23	4.64–10.51	8.16–16.08	20.0–31.80	0.36–0.86
Arithmetic mean	61.78	8.27	10.53	24.53	0.58
Geometric mean	60.30	8.14	10.33	23.82	0.56
Standard deviation	15.42	1.43	2.30	3.46	0.13
pH in 1 mol KCl · dm^{-3} ≥ 6.6					
Range	34.50–84.75	5.58–10.40	5.94–13.71	12.80–29.01	0.24–0.75
Arithmetic mean	54.59	7.91	10.16	19.33	0.46
Geometric mean	53.63	7.75	9.97	18.81	0.44
Standard deviation	10.57	1.65	1.87	4.66	0.14
Content of soluble forms					
pH in 1 mol KCl · dm^{-3} ≤ 6.5					
Range	12.55–42.10	1.63–2.50	0.84–3.22	4.28–11.15	0.34–0.73
Arithmetic mean	21.78	1.96	1.56	7.06	0.48
Geometric mean	20.01	1.94	1.41	6.85	0.47
Standard deviation	10.12	0.31	0.83	3.23	0.11
pH in 1 mol KCl · dm^{-3} ≥ 6.6					
Range	0.87–28.80	0.07–2.58	0.12–2.06	0.30–28.05	0.07–0.67
Arithmetic mean	16.64	1.45	1.01	5.21	0.38
Geometric mean	12.65	0.96	0.80	3.37	0.34
Standard deviation	8.27	0.83	0.53	4.79	0.18

Total contents of the analysed metals and their soluble forms determined in 0.1 mol HCl · dm^{-3} solution were decreasing with increasing pH value. For instance, assuming geometric mean total zinc content in at least slightly acid soils (pH_{KCl} ≤ 6.5) as 100, the total content of this cation in neutral soils (pH_{KCl} ≥ 6.6) was lower by 11 %, whereas its soluble form, respectively by 37 %. Similar relationships occurred, to a bigger or lesser extent, for the other analysed elements.

On the basis of the obtained results, an assessment of the pollution degree of the analysed soils with trace elements was made, according to the guidelines of IUNG [10]. The assessment of pollution of the analysed soil considered the content of floatable particles and the pH value. The studied soils were classified to soils with natural content of heavy metals. Research conducted by Terelak et al [11] revealed that over 80 % of agricultural soils in Poland are characterised by a natural content of heavy metals in the arable layer, whereas in 17 % the content is elevated. Physico-chemical properties of the analysed soils to different extent influenced total contents of trace elements and their soluble forms, as evidenced by simple correlation coefficients (Table 3).

Table 3

Simple correlation coefficients (r) between trace element content in soils and chemical properties of soils

Properties of soils	Zn	Cu	Ni	Pb	Cd
	Total content				
pH in KCl	–0.1551	0.064	–0.2706	–0.3488*	–0.2296
∅ < 0.02 mm	0.2531	0.2343	0.495**	0.2606	0.595***
∅ < 0.002 mm	–0.390**	–0.1839	0.264	0.1168	0.457**
Content of soluble forms					
pH in KCl	–0.169	–0.420**	–0.602***	–0.330*	–0.243
∅ < 0.02 mm	–0.162	0.2143	0.037	0.076	–0.112
∅ < 0.002 mm	–0.358**	–0.075	–0.062	–0.3630*	0.355**

(r) significant at * p = 0.05; ** p = 0.01; *** p = 0.001; n = 44 samples.

The analysed soil pH value (pH_{KCl}) variously influenced total contents of copper, zinc, cadmium and nickel in soils, significantly affecting lead concentrations (negative correlation). A significantly negative correlation was determined between the pH value measured in KCl and concentrations of copper, lead and nickel in soluble forms assessed in 1 mol HCl · dm^{-3} (Table 3).

Concentrations of trace elements in root vegetables. Vegetables are plants accumulating in their tissues considerable amounts of heavy metals which change their chemical composition. The content of selected elements in cultivated vegetables was determined by soil pH, plant species, and analysed plant part [4, 12, 13]. Irrespective of pH value, the content of the studied elements was much higher in tops than in roots (Table 4). If one assumes *eg* geometric mean content of cadmium and lead in parsley roots grown in soils with $pH_{KCl} \leq 6.5$ as 100, then this metal content in its leaves was higher by 64 % and the lead concentration was higher by 36 %. Similar dependencies occurred in the other studied root vegetables.

Trace elements group includes microelements whose are crucial for living organisms because they fulfil some specific functions, e.g. they are catalysts of cell metabolism (Cu, Zn), but also the elements whose physiological role has not been determined yet (Cd and Pb) [14]. Average copper content in plants fluctuated from 5 to 20 mg · kg^{-1} d.m. Its deficit may occur below 5 mgCu · kg^{-1} d.m., while over 20 mg · kg^{-1} d.m. has a toxic effect on plants. Assuming copper content on the level of ≤ 5 mg · kg^{-1} d.m. as deficient, an about 20 % deficiency of this cation was noted in beet roots, celery and parsley roots.

Based on the obtained results, an assessment of vegetable pollution with trace elements was made, assuming the critical values of trace metal concentrations in agricultural products as suggested by IUNG [10]. The guidelines allow for human consumption of agricultural products with the following concentrations of trace elements: $\leq$ 50 mg Zn $\cdot$ kg^{-1}, $\leq$ 20 mg Cu $\cdot$ kg^{-1}, $\leq$ 10 mg Ni $\cdot$ kg^{-1}, $\leq$ 1 mg Pb $\cdot$ kg^{-1} and $\leq$ 0.15 mg Cd $\cdot$ kg^{-1} d.m. The permissible values for usefulness for animal feed are as follows: $\leq$ 100 mg Zn $\cdot$ kg^{-1}, $\leq$ 25 or 50 mg Cu $\cdot$ kg^{-1} (for sheep and for other animals, respectively), $\leq$ 50 mg Ni $\cdot$ kg^{-1}, $\leq$ 10 mg Pb $\cdot$ kg^{-1} and $\leq$ 0.5 mg Cd $\cdot$ kg^{-1} d.m. The root vegetables pollution is presented in Table 4.

The root vegetables only in case of copper and nickel fulfilled the criteria of permissible content for human consumption proposed by IUNG [10].

The permissible Zn content for human consumption was exceeded in roots in 75.6 % of beetroot, in 11.6 % of carrot, in 70.5 % of parsley and in 53.3 % of celery samples. The permissible Zn content was exceeded in tops in 70.7 % of beetroot, in 65.1 % of carrot, in 81.8 % of parsley and in 70.0 % of celery samples. The permissible Zn content for animals was exceeded in tops in 9.8 % of beetroot, in 2.3 % of carrot, in 6.8 % of parsley and in 13.3 % of celery samples.

The permissible Cu and Ni contents for human consumption and for animals were exceeded only in 93.3 % and 6.7 % of celery tops samples, respectively.

The permissible Pb content for human consumption was exceeded in roots in 2.4 % of beetroot, in 6.8 % of carrot, in 11.4 % of parsley and in 10.0 % of celery samples. The permissible Zn content was exceeded in tops in 26.8 % of beetroot, in 68.2 % of carrot, in 40.9 % of parsley and in 73.3 % of celery samples.

The permissible Cd content for human consumption was exceeded in roots in 87.8 % of beetroot, in 95.5 % of carrot, in 54.5 % of parsley and in 90.0 % of celery samples. The permissible Cd content was exceeded in tops in 19.5 % of beetroot, in 20.5 % of carrot, in 65.9 % of parsley and in 16.7 % of celery samples. The permissible Cd content for animals was exceeded in tops in 80.5 % of beetroot, in 77.3 % of carrot, in 27.3 % of parsley and in 83.3 % of celery samples.

Soil pollution with cadmium is an undesirable phenomenon both from biological and ecological perspective. The problem is more complex, because an assessment of cadmium made according to suggested criteria revealed that the cultivated root vegetables do not meet the requirements for usefulness for consumption since they contain over 0.15 mg Cd $\cdot$ kg^{-1} d.m., despite their cultivation in soils with natural or slightly increased content of Cd (Table 4).

Organic and mineral fertilization aims at supplying nutrients to cultivated plants but it should also affect their chemical composition without worsening the crop yield quality. Numerous papers have demonstrated that some amounts of heavy metals which do not affect considerably their soil level are supplied with mineral fertilizers, *eg* phosphorous or multicomponent ones, which are absorbed by the root system in large quantities [7, 15]. Similarly as in Author's own studies, necessity of monitoring trace elements content in vegetables also demonstrated others scientists [16, 17]. Sharma et al [17] stated more Zn, Pb and especially Cd, and less Ni and Cu in carrot roots: 30–112.6 mgZn, 17.75–23.5 mgPb, 0.25–1.25 mgCd, 0.25–5.5 mgNi and 4–6.5 mgCu $\cdot$ kg^{-1} d.m.

Table 4

Assessment of trace element pollution in root vegetables [number of plants]

Content	Beetroot; n = 41 (*Beta vulgaris* L. subsp. *vulgaris*)		Carrot; n = 43 (*Daucus carota* L. subsp. *sativus* Hoffm.)		Parsley; n = 44 (*Petroselinum sativum* Hoffm.)		Celery; n = 30 (*Apium graveolens* L. var. *rapaceum* (Mill.)	
$[\mathrm{mg} \cdot \mathrm{kg}^{-1}]$	Roots	Tops	Roots	Tops	Roots	Tops	Roots	Tops
Zinc								
≤ 50	10	8	38	14	13	5	14	5
≤ 100	31	29	5	28	31	36	16	21
> 100	—	4	—	1	—	3	—	4
Copper								
≤ 20	no critical values were exceeded							28
≤ 25*or 50**	no critical values were exceeded							2
Nickel								
≤ 10	no critical values were exceeded							28
≤ 10	no critical values were exceeded							2
Lead								
≤ 1	40	30	40	13	39	26	27	8
≤ 10	1	11	3	30	5	18	3	22
> 10	no critical values were exceeded							
Cadmium								
≤ 0.15	5	—	1	—	20	3	3	—
≤ 0.5	36	8	42	9	24	29	27	5
> 0.5	—	33	—	34	—	12	—	25

* Critical values for sheep; ** Critical values for other animals.

(on average 55.52 mg, 20.35 mg, 0.62 mg, 5.15 mg and 3.10 mg · kg^{-1} d.m., respectively) than in Author's own studies. In studies of Ngole [18] roots of carrot growing in control object without fertilization contained 2 mgPb · kg^{-1}, and on sludge-amended soil between 2 and 3 mgPb · kg^{-1} d.m. Under those conditions carrot contained 12 mgCu · kg^{-1} and 5–6 mgCu · kg^{-1} d.m., respectively.

On the basis of their investigations, Wisniowska-Kielian and Baran [5] conducted an assessment of vegetables quality based on IUNG criteria [10] and stated that in 11 % of samples zinc concentrations were exceeded (celery and parsley leaves). They also demonstrated that 71 % and 32 % of the analysed samples meet the criteria of consumption usefulness, respectively. Leaves of the analysed vegetables accumulated much bigger quantities of metals than roots. Research conducted by Jasiewicz et al [13] shows that culinary measures such as washing or separating the flesh from the skin reduces the amount of consumed heavy metals. The authors demonstrated that cadmium concentration in radish flesh was six-fold lower than in its skin. Similar results was stated in case of beetroot [19].

The obtained research results point to a necessity to apply agrotechnical measures in the analysed region, which would reduce passing of excessive amounts of heavy metals (particularly cadmium) from soil to plants and therefore to higher organisms. Cadmium poses a hazard to animals and people, because it is toxic and easily absorbed by the organism and has a long biological half-life. Cadmium undergoes a considerable bioaccumulation, so there is a large diversification in its concentrations in animal tissues. Literature data reveal that the problem of cadmium may be solved by increasing pH due to soil liming, increasing the content of organic matter and phosphorus fertilization [3, 20]. In result of these agrotechnical measures, soil ability to bind cadmium increases and therefore its bioavailability decreases. Zaniewicz-Bajkowska et al [21] demonstrated significant decrease of cadmium content in roots of celery and in leek. However, the same Authors [22] show that not always this reduction is so easy to achievement. They found that beetroot cultivated on limed soil contained in roots from 1.08 to 1.14 mgCd · kg^{-1} d.m., and without liming from 1.19 to 1.23 mgCd · kg^{-1} d.m., whereas total content of cadmium in soil was 1.25 and 1.24 mgCd · kg^{-1} d.m., and its soluble forms 0.114 and 0.126 mg Cd · kg^{-1} d.m., respectively. It means that all root samples contained 7.2–8.2-times higher amount of cadmium than permissible in plant material destined for human consumption while soil contained up to twofold bigger amount of this metal than in Authors own study. Under those conditions leaves of beetroot contained 1.27–1.36 mgCd · kg^{-1} and 1.38–1.43 mgCd · kg^{-1}, respectively.

Kachenko and Singh [23] studied heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia stated 2.89–4.23 mgZn, 0.860–1.04 mgCu, < 0.02 mgPb and < 0.05 mgCd · kg^{-1} f.m. of beetroot and 4.45–32.18 mgZn, 0.626–3.85 mgCu, < 0.02–0.630 mgPb and 0.005–0.141 mgCd · kg^{-1} f.m. of parsley. After these data convertion to dry mass Zn, Cu and Pb contents in beetroot were lower than obtained in Authors' own studies, and Cd content was to high. In case of parsley only Cu content was similar to stated in these studies. In Elbagermi et al [24] studies carrot contained 3.61 mgZn, 5.00 mgCu, 0.21 mgNi, 0.21 mgPb and 0.12 mgCd · kg^{-1}, *ie* less than in presented studies.

Conclusions

1. The analysed soils were greatly diversified in regard their pH values measured in 1 mol · dm^{-3} KCl solution (from 4.13 to 7.31), and total trace element content (5.65–18.28 mgCu · kg^{-1}, 54.6–227.6 mgZn · kg^{-1}, 0.52–2.92 mgCd · kg^{-1}).

2. Contents of the analysed trace elements in root vegetables cultivated in the Miechowski county ranged widely depending on the soil pH, content and form of elements, species, and analysed plant part.

3. Taking into consideration heavy metal content was stated that the root vegetables (both roots and tops) did not fulfil criteria of usefulness for human consumption (according to IUNG) because of excess of copper and nickel in 0.6 %, lead in 29.4 %, zinc in 66.1 %, and especially of cadmium in 89.9 % of samples, despite their being cultivated in soils with natural Cd content.

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OCENA STOPNIA ZANIECZYSZCZENIA GLEB ORAZ WARZYW KORZENIOWYCH PIERWIASTKAMI ŚLADOWYMI

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Abstrakt: Badania dotyczyły określenia stopnia zanieczyszczenia gleb oraz warzyw korzeniowych uprawianych na cele konsumpcyjne pierwiastkami śladowymi na terenie powiatu miechowskiego. Zebrane gleby były zróżnicowane pod względem zawartości części spławialnych, iłu koloidalnego, materii organicznej, wartości pH, całkowitej zawartości pierwiastków śladowych oraz ich form rozpuszczalnych w roztworze 0,1 mol HCl $\cdot$ dm^{-3}.

O całkowitej zawartości pierwiastków śladowych, jak i ich formach rozpuszczalnych w badanych glebach decydował odczyn gleb. Średnie geometryczne całkowite zawartości metali ciężkich w badanych glebach wynosiły: 55,08 mgZn $\cdot$ kg^{-1}, 8,08 mgCu $\cdot$ kg^{-1}, 10,05 mgNi $\cdot$ kg^{-1}, 19,05 mgPb $\cdot$ kg^{-1} i 0,46 mgCd $\cdot$ kg^{-1}. Zanieczyszczenie badanych gleb metalami ciężkimi oceniono w oparciu o ramowe wytyczne dla rolnictwa opracowane przez IUNG. Pod tym względem 44 badane próbki glebowe zaliczono do gleb o naturalnej zawartości metali ciężkich. O zawartości pierwiastków śladowych w uprawianych warzywach korzeniowych decydował gatunek, analizowana część rośliny oraz pH gleby. Zawartość tych pierwiastków była znacznie większa w częściach nadziemnych niż w korzeniach. Przyjmując np. średnią geometryczną zawartość kadmu i ołowiu w korzeniach pietruszki wyrosłych na glebach o pH$_{\text{KCl}}$ $\leq$ 6,5 za 100, zawartość kadmu w naci była większa o 64 %, a ołowiu o 36 %. Na podstawie uzyskanych wyników oceniono zawartości metali śladowych w warzywach korzeniowych, przyjmując ich poziomy krytyczne w płodach rolnych opracowane przez IUNG. Biorąc pod uwagę te kryteria stwierdzono, że wszystkie próbki korzeni spichrzowych badanych warzyw spełniały wymagania przydatności konsumpcyjnej dla ludzi pod względem zawartości miedzi i niklu, a większość pod względem zawartości ołowiu. Natomiast 7,6% próbek nie spełniało tych wymagań z powodu nadmiernej zawartości ołowiu (> 1 mg $\cdot$ kg^{-1} s.m.), 52,5% cynku (> 50 mg $\cdot$ kg^{-1} s.m.), a aż 81,6 % próbek z powodu nadmiaru kadmu (> 0,15 mg $\cdot$ kg^{-1} s.m.), pomimo że warzywa były w większości uprawiane na glebach o naturalnej zawartości tych metali. Nadmierne zawartości miedzi i niklu zanotowano tylko w 1,3 % próbek, ołowiu w 51,3 %, cynku w 79,7 %, a kadmu aż w 98,1 % próbek naci tych warzyw, w tym 7,6 % próbek nie spełniało wymagań paszowych pod względem zawartości cynku, a aż 65,8 % – kadmu.

Z ogółu próbek korzeni i naci nie spełniało wymagań konsumpcyjnych z powodu nadmiernej zawartości miedzi i niklu tylko 0,6 % próbek, ołowiu 29,4 % próbek, cynku 66,1 %, a kadmu aż 89,9 % próbek, w tym w 3,8 % próbek wykazywało przekroczenia dopuszczalnych zawartości Zn i 32,9% Cd w paszach.

Słowa kluczowe: gleba, warzywa korzeniowe, zawartość Cu, Zn, Cd, Pb, Ni

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THE ADSORPTION OF PENDIMETHALIN BY PEATS AND LAKES BOTTOM SEDIMENTS

ADSORPCJA PENDIMETALINY NA TORFACH I OSADACH DENNYCH JEZIOR

Abstract: The paper presents results of an experimental research on the influence of the adsorbent type on the adsorption of pendimethalin and water/peat index and water/bottom sediment index (K_d and K_{OC}). The research was carried out in a laboratory using samples of bottom sediment and peat of various organic carbon contents. The experiment involved herbicide of Panida 330 EC containing 330 g of pendimethalin in 1 dm^3 of preparation.

According to the research, there is a strong relationship between adsorption and time emulsion of pesticide remains in contact with peat and bottom sediment samples. Additionally, results indicate that adsorption of pendimethalin involves two phases. The first phase is fast and non-linear, whereas the second one slow and linear. The 24 hour contact and 10 hour contact in the case of an increased content of adsorbent by 150 % between herbicide emulsion and peat/bottom sediment samples enabled to reach an adsorption equilibrium in the active substance. The content of organic carbon in peat and bottom sediment samples was decisive as regards time of non-linear phase of pendimethalin adsorption.

Keywords: herbicide, adsorption, peat, lake bottom sediment

Introduction

For many years, despite numerous controversies related to their negative impact on the environment, crop protection chemicals have been the most effective and modern

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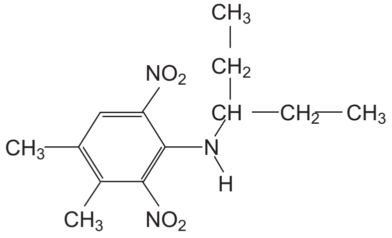
method of counteracting threats to the yield from biotic factors [1]. Due to their common application and long half-time in the natural environment, remains of those chemicals can now be found in all segments of the natural environment, including water, soil, bottom sediments, air, plants and living organisms [2]. Apart from its direct threat, the accumulation of pesticides in the environment promotes their movement inside and between ecosystems. A natural storage of all types of contamination in ecosystems, including pesticides, is soil. Adsorption of pesticides by soil plays an important role in their transport and movement in the environment. It is assumed that the sorption of xenobiotics involves various mechanisms, *eg* formation of hydrogen bonds – weak surface interactions or strong ionic interactions [3]. In the case of pesticides, Gevao et al [4] have distinguished van der Waals interactions, π-electron interactions and covalent bonds.

According to the literature, the process of pesticides adsorption involves two phases [5–8]. The first one is a macroscopic process (macro sorption) which includes surface sorption. For those processes the equilibrium constant is reached relatively fast. The second phase requires longer contact between pesticide and soil, and involves a microscopic process (micro sorption), related to diffusion of pesticides into inner active layers. Contamination is either enclosed in 3D structure of macromolecules of the organic matter or in interpocket space of clay minerals.

The research aimed at defining the influence of different types of adsorbent of various organic carbon content on kinetics of pendimethalin adsorption – an active substance in the Panida 330 EC preparation, and determining water/peat and water/bottom sediment indices (K_d and K_{OC}) for the linear phase (micro sorption) of the process.

Material and methods

The experiment used Panida 330 EC herbicide (*emulsifiable concentrate*) which contained pendimethalin as a biologically active substance (Fig. 1).



$C_{13}H_{19}N_3O_4$
$M = 281.31\ g \cdot mol^{-1}$
N-(1-ethyloprophyl)-3,4-dimethyl-2,6-dinitroaniline

Fig. 1. Structural formula of pendimethalin

It is a selective soil-applied herbicide which migrates into a plant through its roots and leaves preventing mitotic division of cells and growth of weed seedlings. The herbicide is commonly used to eradicate weeds from a number of crops [9–11].

The research on adsorption of dinitroaniline derivative used lyophilised samples of bottom sediments from lake Kociolek (sample O1) and lake Smiadowo (sample O2) and dry surface samples of peat from Jablonka fen (sample T1) and Pod Dolnym Plajem fen (sample T2). In all samples examined the content of water did not exceed 12 %. Lakes Kociolek and Smiadowo, situated in West Pomerania, are lobelia lakes of volatile morphometric parameters. Jablonka fen situated in the Orawsko-Nowotarska basin, whereas Pod Dolnym Plajem fen in the Babiogorski National Park. In both fens, soil has undergone different pedogenic processes. The following assessments were made in the analysed soils: pH (by potentiometric method in H_2O and 1 mol · dm^{-3} KCl solution), organic carbon and total nitrogen content on LECO CNS 2000 apparatus. Physico-chemical properties of the both adsorbents are presented in Tables 1 and 2. The content of organic carbon was the main criterion for selecting samples of bottom sediment and peat.

Table 1

Physico-chemical properties of peat samples

Physico-chemical properties / Peat samples	Geographical location	pH		C_{org}	N_{tot}	C_{org}/N_{tot}
		H_2O	KCl	[g · kg^{-1}]		
Jablonka fen (T1)	N 49°29′54.4″ E 19°40′51.6″	5.8	5.1	344	20.0	17.2
Pod Dolnym Plajem fen (T2)	N 49°35′43.5″ E 19°30′15.1″	6.3	5.7	264	22.6	11.5

Table 2

Physico-chemical properties of bottom sediment samples

Physico-chemical properties / Bottom sediment samples	Geographical location	pH		C_{org}	N_{tot}	C_{org}/N_{tot}
		H_2O	KCl	[g · kg^{-1}]		
Lake Kociolek (O1)	N 53°56′30″ E 16°41′	4.4	3.8	220	16.0	13.7
Lake Smiadowo (O2)	N 51°37′ E 16°34′	5.0	4.5	118	11.0	10.8

Pendimethalin adsorption tests were performed at 20 °C in dynamic conditions, where the ratio of peat/bottom sediment mass to the volume of the solution was: 1:10 for sample T2 (2.5 g peat + 25 cm^3 pendimethalin solution), and 1:25 for samples O1, O2 and T1 (1.0 g peat/bottom sediment + 25 cm^3 pendimethalin solution). While preparing samples, 2.5 g of sample T2 and 1.0 g of O1, O2 and T1 were placed on a laboratory scales. Samples were weighted in conical flasks with cut of 50 cm^3. 25 cm^3 pendimethalin solution of 0.2 mg · cm^{-3} was added to the experimental material. For each peat/bottom sediment sample ten (10) measurement points were prepared in three consecutive series. The samples were closed with corks and mixed in laboratory shakers. After shaking, the samples were centrifuged at each time point for 5 minutes at 4000 rev · min^{-1}, and the pendimethalin solution underwent extraction with chloroform (5 cm^3) and spectrophotometric analysis was applied to measure the value of absorbance at wavelength of 430 nm. The quantitative interpretation of the active substance tested was performed using a rating curve.

The examining of the pendimethalin adsorption kinetics in peat/bottom sediment samples involved measurements after 0, 5, 15, 30, 45, 60, 90, 120, 180, 540 and 1440 minutes of contact between the pendimethalin solution and the above mentioned adsorbents.

While taking into consideration the difference between the initial concentration (C_0) and equilibrium concentration (C_r), and the volume of the solution and the mass of peat/bottom sediment samples, calculations were made to determine the adsorption (x/m) of pendimethalin in peat and bottom sediment samples analysed according to formula (1) [8]:

$$\frac{x}{m} = \frac{V \cdot (C_0 - C_r)}{m} \tag{1}$$

where: x – mass of adsorber in peat/bottom sediment [mg],
m – mass of peat/bottom sediment [g],
V – volume of solution used for measurement [$\mathrm{dm^3}$],
C_0 – concentration of component in initial solution [$\mathrm{mg \cdot dm^{-3}}$],
C_r – concentration of component in adsorption equilibrium solution [$\mathrm{mg \cdot dm^{-3}}$].

The experimental values of adsorption and equilibrium concentration were used to calculate (dispersion) water/peat and water/bottom sediment ratios, K_d and K_{OC} respectively, while taking into consideration the content of organic carbon in adsorbents for the active substance (a.s.). K_d and K_{OC} for the analysed pendimethalin peat/sediment system were calculated for the linear phase (micro sorption) of the adsorption process. The analysis times for bottom sediments, peat sample from Jablonka fen and peat sample from Pod Dolnym Plajem fen were respectively 24 and 10 hours for the adsorption process concerned. The value of K_d was calculated based on formula (2) [12, 14]:

$$K_d = \frac{\text{mg a.s./kg adsorbent}}{\text{mg a.s./dm}^3\text{ water}} \tag{2}$$

Resulting values of K_d are translated into K_{OC} according to equation (3) [13, 14]:

$$K_{OC} = \frac{K_d \cdot 100\%}{C\%} \tag{3}$$

Results

The relationship between adsorption of pendimethalin and contact time is presented in Fig. 2. Resulting curves show changes of the pendimethalin adsorption rate. Regardless the peat/bottom sediment system used, the geometry of curves indicates relationship between the parameters and a clear dual phase (non-linear and linear) adsorption process.

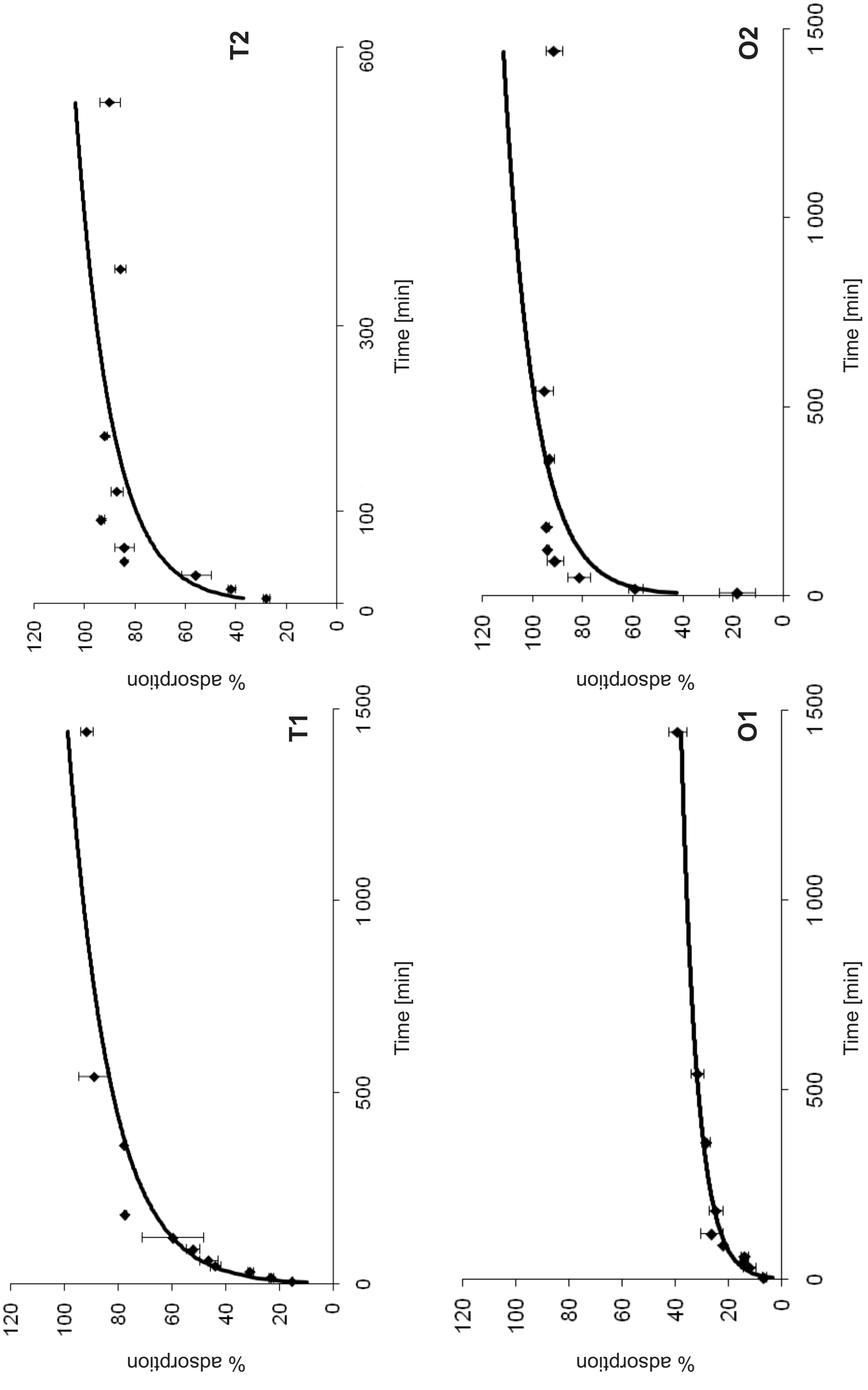


Fig. 2. Kinetics of pendimethalin adsorption in peat samples (T1, T2) and bottom sediments samples (O1, O2)

Depending on the type of adsorbent (peat, bottom sediment), the linear relationship between the volume of herbicide adsorbed and time of contact with adsorbent is reached in 60 to 180 minutes. The linear phase is reached much faster for samples of bottom sediments: from 90 minutes in the case of O2 sample of the lowest organic carbon content (C_{org} =118 g · kg^{-1}) to 120 minutes in the case of O1 sample (C_{org} = 220 g · kg^{-1}). The non-linear phase of the pendimethalin adsorption was significantly prolonged to 180 minutes for sample T1 of 344 g · kg^{-1} organic carbon content. In the case of T2, the quantity of adsorbent was increased to 2.5 g which resulted in reaching the linear phase of the process much faster, namely in just 60 minutes.

According to the analysis, pendimethalin shows significant adsorption capacity. In the case of bottom sediment samples, the highest adsorption values (4.01–4.20 mg · g^{-1}), for the linear phase of the process, were recorded for sample O2. Between 90 to 1440 minutes were sufficient to adsorb 91.07 ± 3.24 % to 95.45 ± 3.44 % of the active substance applied. Adsorption of pendimethalin in bottom sediment samples was not correlated with the content of organic carbon. Sample O1 showed nearly 100 % higher organic carbon content in comparison with sample O2; *x/m* values were significantly lower. The linear adsorption phase involved adsorption of 24.73 ± 2.78 % to 39.45 ± 3.48 % of pendimathalin, and adsorption was at the level of *x/m* = 1.08–1.72 mg · g^{-1}.

The peat samples used showed considerable pendimethalin adsorption capacity. During the linear phase, sample T1 adsorbed 77.66 ± 0.53 % to 91.86 ± 0.53 % of the active substance within 180 to 1440 minutes. For the time span concerned, pendimethalin adsorption values calculated varies from 3.41 to 4.05 mg · g^{-1}. The volume of adsorbent used for testing has significant influence on the effectiveness of the adsorption process, in particular during the initial non-linear phase. Pendimethalin adsorption results obtained for the increased dose of the adsorbent in sample T2 were from 0.49 to 1.65 mg · g^{-1}. In the linear phase, the adsorption of substance analysed was from 84.44 ± 2.53 % to 93.46 ± 1.05 % per every 2.5 g of sample T2. An increased dose of the adsorbent shortened the non-linear phase of the process and expedited reaching the adsorption equilibrium. As regards peat samples, a major relationship was determined between the adsorption process and the content of organic carbon. For sample T1 of increased organic carbon content (C_{org} = 344 g · kg^{-1}), *x/m* values of pendimethalin were by 22.89 to 59.43 % higher if compared with pendimethalin *x/m* for sample T2 (C_{org} = 264 g · kg^{-1}).

Table 3

Values of water/peat and water/bottom sediment pendimethalin indices (K_d, K_{OC})

Sampling points location	K_d	K_{OC}
	[$dm^3 \cdot kg^{-1}$]	
Lake Kociolek (O1)	16.0	73
Lake Smiadowo (O2)	267.1	2271
Jablonka fen (T1)	282.2	820
Pod Dolnym Plajem fen (T2)	9.7	90

According to data presented in Table 3, we can see that the highest value of K_d was obtained for sample T1 of the highest organic carbon content, whereas sample O2, of the lowest organic carbon content, showed the highest K_{OC}. No relationship was determined between the value of those adsorption indices and organic carbon content in adsorbent samples.

Conclusions

1. The research shows that there is a direct relationship between adsorption and the time herbicide emulsion remains in contact with peat and bottom sediment samples.
2. Adsorption of pendimethalin contained in Panida 330 EC involves two phases: macro adsorption – a non-linear phase in which the equilibrium is achieved relatively fast, and micro adsorption – a linear phase in which reaching the equilibrium takes more time.
3. The 24 hour contact and 10 hour contact in the case of increased content of adsorbent by 150 % between herbicide emulsion and peat/bottom sediment samples led to an adsorption equilibrium in the active substance.
4. The content of organic carbon in peat and bottom sediment samples was decisive as regards time of the non-linear phase of pendimethalin adsorption.

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ADSORPCJA PENDIMETALINY NA TORFACH I OSADACH DENNYCH JEZIOR

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Abstrakt: Przedstawiono wyniki badań doświadczalnych nad wpływem rodzaju adsorbentu na szybkość adsorpcji pendimetaliny oraz wartość współczynników podziału woda/torf oraz woda/osad denny (K_d i K_{OC}). Badania przeprowadzono w warunkach laboratoryjnych z zastosowaniem próbek osadów dennych i torfów o różnej zawartości węgla organicznego. W doświadczeniu wykorzystano herbicyd Panida 330 EC zawierający 330 g pendimetaliny w 1 dm^3 preparatu.

Badania wykazały, że istnieje ścisła zależność adsorpcji od czasu kontaktu emulsji pestycydu z próbkami torfów i osadów dennych. Uzyskane wyniki wskazują ponadto, że adsorpcja pendimetaliny zachodzi w dwóch etapach. Pierwszy etap jest szybki – nieliniowy, drugi wolny – liniowy. 24-godzinny czas kontaktu, a w przypadku zwiększenia ilości adsorbentu o 150 %, 10-godzinny czas kontaktu emulsji herbicydu z próbkami torfów/osadów dennych umożliwił osiągnięcie stanu równowagi adsorpcyjnej badanej substancji aktywnej. Zawartość węgla organicznego w próbkach torfowych i osadów dennych miała decydujący wpływ na czas trwania nieliniowego etapu adsorpcji pendimetaliny.

Słowa kluczowe: herbicyd, adsorpcja, torfy, osady denne jezior

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MACROPHYTES AS INDICATORS OF HEAVY METALS BIO-ACCUMULATION IN UPPER NAREW RIVER

MAKROFITY JAKO WSKAŹNIKI BIOPRZYSWAJALNOŚCI METALI CIĘŻKICH W GÓRNEJ NARWI

Abstract: The study aimed at evaluating the cadmium, nickel, zinc, copper, cobalt, chromium and lead contents in bottom sediments, as well as roots and above ground parts of *Carex elata* and *Acorus calamus* in upper Narew River. Studies were carried out in summer 2008 at 10 measurement points localized on Narew River (Bondary, Ploski, Doktorce, Rzedziany, Uhowo, Bokiny Zlotoria, Siekierki and Tykocin). The metal concentrations were determined by means of AAS technique. Calculated bio-accumulation coefficients for roots of examined plants were following: *Carex elata* Co > Cu > Zn > Cd > Ni > Pb = Cr while for *Acorus calamus* Co > Cu > Zn > Cd > Ni > Cr > Pb. It can be supposed that household activity, including influences of a local transport and surface runoffs, were the main sources of examined metals deposited in bottom sediments and aquatic plants of upper Narew River. Studied plant material and bottom sediments were only slightly contaminated with cadmium.

Keywords: heavy metals, macrophytes, Narew River

Introduction

The problem of aquatic environment contamination with heavy metals is still serious despite of numerous activities associated with limitations of anthropogenic emission of these elements [1–4]. Evaluation of the aquatic environment quality includes monitoring of heavy metals contents in bottom sediments, as well as in flora and fauna living in water reservoirs or flows [5–10]. They may be a valuable source of information on qualitative and quantitative changes within rivers [11–13].

The aim of present study was to evaluate the cadmium, nickel, zinc, copper, cobalt, chromium and lead contents in bottom sediments, as well as roots and above ground parts of *Carex elata* and *Acorus calamus* in upper Narew River.

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Material and methods

The study was performed in summer 2008 at 10 measurement points localized on Narew River (Bondary, Ploski, Doktorce, Rzedziany, Uhowo, Bokiny Zlotoria, Siekierki and Tykocin). Plant material and bottom sediments were experimental material subjected to determinations of total contents of cadmium, nickel, zinc, copper, chromium, cobalt and lead, as well as their soluble forms. Tussock sedge (*Carex elata*) and sweet flag (*Acorus calamus*) grew at all studied points were test plants. The bottom sediment was collected from the shore zone where the sedimentation of suspended material occurs. Samples were air-dried and sieved through a polyethylene screen (0.2 mm mesh). Fraction of < 200 μm particle diameter was used for study, because it is applied in works associated with geochemical mapping [14]. At the same time, roots and above ground parts of tussock sedge and sweet flag were collected. After drying, each sample (roots and above ground parts) were ground using agate mill. Then, bottom sediments and plant material was digested in nitric acid in a hermetic microwave system CEM Mars-5. The bottom sediments samples were also subjected to extraction of metals soluble forms in cool 1 mol · dm^{-3} HCl solution [15]. Applied hydrochloric acid is one of the most commonly used to isolate the non-residual metal fraction from solid samples [16]. In addition, according to Sutherland [17] and Frankowski et al [16], diluted HCl is the most suitable eluent for determination of anthropogenic sources of metals in solid samples. The metals concentrations were determined by means of AAS technique (spectrophotometer Varian SpectraAA-100).

Classification of water sediments in Poland on a base of geochemical criteria was applied to evaluate the level of sediment contamination with heavy metals [18] and threshold values taking into account the detrimental effect of pollutants accumulated in sediments on aquatic organisms [19]. The results on the content of tested metals in the upright sedge (*Carex elata*) and sweet flag (*Acorus calamus*) are based on the dry weight of plants and compared to the literature data relating to a dry weight of plants. The physiological norm of metals contents for plants was quoted after data presented by [20].

Statistica 7.1 software was used for statistical analysis of test results: arithmetic mean, standard deviation, median and also Spearman correlation coefficients between content of metals in the bottom sediments and plants, were calculated.

Results and discussion

Concentrations of studied metals in collected bottom sediments samples from upper Narew River revealed variability due to the level of the sediment dispersion, as well as the localization of the measure point. It referred both to the total and labile forms of analyzed heavy metals. Sediments were characterized by following arithmetic mean and standard deviation (Table 1) values of their total contents: 1.52 ± 0.07 mgCd · kg^{-1}, 14.2 ± 1.45 mgPb · kg^{-1}, 47.5 ± 15.36 mgZn · kg^{-1}, 14.8 ± 3.99 mgCr · kg^{-1}, 11.9 ± 0.99 mgNi · kg^{-1}, 3.5 ± 1.12 mgCu · kg^{-1} and 2.6 ± 0.18 mgCo · kg^{-1} d.m. From a point of view of the environmental pollution, the soluble portion of metals is very important,

Table 1

Heavy metals contents in bottom sediments

River	Nearest locality	Cd		Pb		Zn		Cr		Ni		Cu		Co	
		Heavy metals contents in bottom sediments [mg · kg^{-1} d.m.]													
		A*	B**	A	B	A	B	A	B	A	B	A	B	A	B
Narew	Tykocin	1.51	0.36	14.1	4.1	59.1	24.3	25.1	4.3	12.7	1.1	5.7	1.6	2.3	0.9
Narew	Siekierki	1.46	0.18	13.1	5.4	48.9	18.7	17.1	2.5	10.1	1.2	3.2	0.6	2.6	0.8
Narew	Zlotoria	1.54	021	13.9	4.1	36.4	20.7	13.9	0.6	10.6	0.9	2.9	1.2	2.9	0.6
Narew	Rzedziany	1.53	0.74	14.3	6.4	30.1	21.7	10.8	0.8	12.3	2.1	3.7	1.3	2.5	0.7
Narew	Bokiny	1.58	0.19	14.2	6.9	77.8	17.2	14.1	0.7	12.3	1.2	2.9	1.1	2.8	0.8
Narew	Uchowo	1.63	0.55	18.2	7.1	61.9	18.6	14.5	0.9	13.4	2.4	5.3	2.1	2.4	1.1
Narew	Doktorce	1.37	0.15	13.4	4.5	47.8	19.7	14.4	0.7	12.1	1.1	2.9	1.0	2.5	0.6
Narew	Ploski	1.54	0.42	14.1	7.3	33.9	18.9	11.6	0.5	11.3	0.8	3.2	0.5	2.6	0.8
Narew	Narew	1.46	0.93	13.4	4.6	47.3	19.1	13.2	0.6	12.4	1.1	3.3	1.1	2.4	1.1
Narew	Bondary	1.53	1.02	13.6	5.8	31.6	18.9	13.5	0.7	12.1	1.2	2.1	0.5	2.5	0.8
Arithmetic mean		1.52	0.40	14.2	5.6	47.5	19.8	14.8	1.2	11.9	1.3	3.5	1.1	2.6	0.8
Standard deviation		0.07	0.32	1.45	1.25	15.36	2.00	3.99	122	0.99	0.52	1.12	0.50	0.18	0.17
Median		1.54	0.39	14.4	5.2	48.0	18.9	14.4	0.6	12.1	1.0	3.3	1.2	2.6	0.8

* A – decomposition in HNO_3 and H_2O_2; ** B – extracted with 1 mol · dm^{-3} HCl solution.

because due to their mobility, metals can be desorbed from sediments to water, as well as be accumulated in benthos organisms [15, 20]. Performed study revealed following arithmetic mean and standard deviation (Table 1) values for labile forms: cadmium – 0.40 ± 0.32 $\mathrm{mgCd \cdot kg^{-1}}$, 5.6 ± 1.25 $\mathrm{mgPb \cdot kg^{-1}}$, 18.9 ± 2.00 $\mathrm{mgZn \cdot kg^{-1}}$, 1.2 ± 1.22 $\mathrm{mgCr \cdot kg^{-1}}$, 1.3 ± 0.52 $\mathrm{mgNi \cdot kg^{-1}}$, 1.1 ± 0.50 $\mathrm{mgCu \cdot kg^{-1}}$ and 0.8 ± 0.17 $\mathrm{mgCo \cdot kg^{-1}}$ d.m.

Result analysis indicated that the highest level of total contents and labile forms was found for zinc and lead, whereas the lowest concentrations were determined in the case of cadmium and cobalt. The ratios of labile to total forms of heavy metals concentrations in studied bottom sediments and expressed as a percentage could be lined up in the following sequence: Zn > Pb > Cu > Co > Cd > Ni > Cr. It illustrates the mobility of examined metals as well as their anthropogenic origin. Studies revealed relatively low share of chromium soluble form in its total content that in majority of examined samples, was from 4 to 10 %. Kabata-Pendias [21] reported that chromium is one of the least mobile trace elements in a natural environment. In not contaminated bottom sediments, it occurs in a stable form in 84 %. Zinc is one of the most mobile metals in a natural environment, which was also confirmed by numerous studies; its soluble form share in the total content of the bottom sediments ranged from 30 % to 80 %. The lead and copper labile forms in their total contents made up about 30 % to 40 % in examined sediments, while those of cobalt and cadmium from 25 % to 30 %, and nickel from 8 % to 18 %, because it readily forms quite durable chelate and compounds, as well as complex cations and anions. Analysis of study results from bottom sediments in upper Narew River and their comparison to sediment classification in Poland on a base of geochemical criteria [18, 19], it was found that copper and zinc contents in Zlotoria, Rzedziany, Doktorce, Ploski, Narew and Bondary localities were at the level of geochemical background, while other metals (lead, nickel, chromium and cobalt) should be classified to the I class as not contaminated sediments (Table 2).

Table 2

Geochemical classification of sediments from upper Narew River

Nearest locality	Classification of metal content in sediments						
	Cd	Pb	Zn	Cr	Ni	Cu	Co
Tykocin	II	I	I	I	I	Background	I
Siekierki	II	I	I	I	I	Background	I
Złotoria	II	I	Background	I	I	Background	I
Rzedziany	II	I	Background	I	I	Background	I
Bokiny	II	I	I	I	I	Background	I
Uchowo	II	I	I	I	I	Background	I
Doktorce	II	I	Background	I	I	Background	I
Ploski	II	I	Background	I	I	Background	I
Narew	II	I	Background	I	I	Background	I
Bondary	II	I	Background	I	I	Background	I

Source: own work based on the Bojakowska and Sokołowska [18] and Bojakowska [19].

Cadmium was the exception, because a slight exceeding the I geochemical class occurred (Table 2). Such concentrations result mainly from the anthropogenic factors, due to which it penetrates along with the surface runoff from cultivated fields with wrong phosphorus fertilizing management [20], as well as along with the sewage; transport is also a significant source of cadmium contamination [18]. Koc et al [22] and Skorbilowicz [23] argue that the modification of chemical composition of water flowing within the catchment of Narew River results primarily from structure of agricultural performance of its surface. In addition, water of Narew River is enriched in contaminants from urban settlements and storm waters from both rural and urban areas. Mioduszewski [24] and Banaszuk [25] note that relatively intensive agriculture carried out in the vicinity of the valley, meadow management on part of the bogs, and processes of organic formations decay that take place in the upper Narew River cause significant changes in migration processes within the landscape.

Contents of heavy metals at aquatic plants can be one of the indicators of anthropopresure influences on natural environment. Heavy metal contents at aquatic plants reflect their bio-available forms concentrations in a natural environment as well as valuable complement of bottom sediments studies. Values of metal arithmetic mean and standard deviation in roots of *Carex elata* (Table 3) were: 1.9 ± 0.25 mgCd · kg^{-1}, 7.6 ± 1.04 mgPb · kg^{-1}, 78.2 ± 12.79 mgZn · kg^{-1}, 7.1 ± 3.66 mgCr · kg^{-1}, 8.6 ± 0.98 mgNi · kg^{-1}, 6.2 ± 1.98 mgCu · kg^{-1} and 9.2 ± 0.69 mgCo · kg^{-1} d.m., while in roots of *Acorus calamus*: 2.1 ± 0.07 mgCd · kg^{-1}, 7.7 ± 1.17 mgPb · kg^{-1}, 67.4 ± 15.23 mgZn · kg^{-1}, 8.9 ± 3.9 mgCr · kg^{-1}, 9.0 ± 1.67 mgNi · kg^{-1}, 5.4 ± 1.72 mgCu · kg^{-1} and 9.0 ± 0.93 mgCo · kg^{-1} d.m. (Table 4). Values of arithmetic mean and standard deviation for studied metals at above ground parts of test plants were slightly different: *Carex elata* (Table 3): 1.4 ± 0.28 mgCd · kg^{-1}, 6.8 ± 0.96 mgPb · kg^{-1}, 38.7 ± 5.94 mgZn · kg^{-1}, 4.8 ± 0.92 mgCr · kg^{-1}, 5.6 ± 1.31 mgNi · kg^{-1}, 3.1 ± 0.64 mgCu · kg^{-1} and 6.3 ± 0.75 mgCo · kg^{-1} d.m., whereas *Acorus calamus*: 1.4 ± 0.29 mgCd · kg^{-1}, 7.8 ± 1.13 mgPb · kg^{-1}, 56.8 ± 17.83 mgZn · kg^{-1}, 5.6 ± 3.33 mgCr · kg^{-1}, 4.4 ± 0.67 mgNi · kg^{-1}, 3.8 ± 0.98 mgCu · kg^{-1} and 6.7 ± 0.85 mgCo · kg^{-1} d.m. (Table 4).

Cadmium and lead are dangerous and toxic to most of life forms and more available to aquatic organisms. Distribution of these metals within the plant depends on a number of factors, including the form of the metal (ion, complex), presence of other metals, as well as the species and individual characteristics, and even a plant organ. The root usually has a higher content than shoot [26, 27]. In majority of analyzed cases, studies upon Cd and Pb confirmed that fact. According to Kabata-Pendias [28], the Cd contents in plants are very diverse and most often are in the range of 0.05–0.2 mg · kg^{-1}. The toxicity symptoms occur at amounts around 5–10 mg · kg^{-1} for sensitive plants, and 10–30 mg · kg^{-1} for resistant plants. In all samples, it was found that concentration of a given metal in the test plants amounted to over 0.2 mg · kg^{-1}.

The average value of bioaccumulation coefficient for studied plants in the case of Cd was 1.3 ± 0.29 (Table 5).

Contents of Pb found in *Carex elata* and *Acorus calamus* did not exceed 15 mg · kg^{-1} (Table 3 and 4), while toxic content according to Kabata-Pendias and Pendias [20] is 30

Table 3

Heavy metals contents in *Carex elata*

River	Nearest locality	Cd		Pb		Zn		Cr		Ni		Cu		Co	
		Heavy metals contents in *Carex elata* [mg · kg^{-1} d.m.]													
		P*	R**	P	R	P	R	P	R	P	R	P	R	P	R
Narew	Tykocin	1.7	2.6	6.9	7.3	45.1	94.6	4.9	7.7	5.3	8.6	3.1	4.8	5.2	9.9
Narew	Siekierki	1.3	1.8	6.3	6.1	34.6	93.7	5.2	15.9	7.1	7.3	2.4	8.8	6.7	8.6
Narew	Złotoria	1.3	2.2	7.5	8.9	39.2	83.7	3.7	7.2	7.2	9.7	3.1	6.7	7.1	9.3
Narew	Rzedziany	1.3	1.8	8.3	7.8	39.4	50.8	5.1	9.3	4.9	8.1	3.7	4.9	4.9	9.8
Narew	Bokiny	2.2	1.8	7.1	7.1	48.1	82.1	3.8	4.5	5.1	9.1	3.7	7.7	6.6	10.2
Narew	Uchowo	1.3	1.8	6.9	9.4	44.7	67.6	4.1	3.3	5.2	8.2	3.5	9.9	6.9	9.1
Narew	Doktorce	1.4	1.9	6.4	7.1	32.1	75.7	3.9	3.8	4.8	10.6	3.3	5.1	5.9	8.9
Narew	Ploski	1.3	1.9	6.3	7.5	29.5	80.7	4.9	6.9	7.7	8.9	1.6	3.9	6.7	7.9
Narew	Narew	1.4	2.0	8.1	8.3	36.1	72.1	6.7	5.2	3.8	8.7	3.4	5.1	6.9	8.6
Narew	Bondary	1.4	1.9	6.4	6.4	38.1	80.5	5.3	6.8	4.4	8.3	3.1	5.2	6.3	9.3
Arithmetic mean		1.4	1.9	6.8	7.6	38.7	78.2	4.8	7.1	5.6	8.58	3.10	6.2	6.3	9.2
Standard deviation		0.28	0.25	0.96	1.04	5.94	12.79	0.92	3.66	1.31	0.98	0.64	1.98	0.75	0.69
Median		1.4	1.9	6.9	7.3	38.6	80.7	4.8	6.9	5.5	8.2	3.3	5.2	6.7	9.1

* P – Heavy metals contents in above ground parts; ** R – Heavy metals contents in roots.

Table 4

Contents of heavy metals in *Acorus calamus*

River	Nearest locality	Cd		Pb		Zn		Cr		Ni		Cu		Co	
		Heavy metals contents in *Acorus calamus* [mg · kg^{-1} d.m.]													
		P*	R**	P	R	P	R	P	R	P	R	P	R	P	R
Narew	Tykocin	1.1	2.2	6.1	6.5	39.8	58.3	5.1	7.8	4.4	8.3	3.8	3.6	6.8	8.1
Narew	Siekierki	1.9	1.9	7.9	7.9	74.2	87.6	7.2	19.2	5.5	10.3	4.8	8.1	6.9	9.2
Narew	Złotoria	1.4	2.1	8.7	8.2	58.9	65.2	3.8	11.7	4.6	12.6	3.5	8.9	6.1	7.3
Narew	Rzedziany	1.3	2.2	8.8	8.9	52.6	61.3	4.2	7.6	4.9	9.5	3.7	4.9	6.8	8.2
Narew	Bokiny	1.8	2.3	6.7	6.4	44.6	58.2	3.9	7.5	4.2	9.3	3.7	5.1	5.9	9.6
Narew	Uchowo	1.7	1.9	9.7	8.5	56.1	66.8	4.4	7.2	3.5	8.8	3.1	5.2	6.7	9.9
Narew	Doktorce	1.5	2.3	7.8	8.9	53.4	65.1	4.1	7.3	3.9	7.8	2.2	4.1	6.8	8.7
Narew	Ploski	1.2	2.4	8.1	8.3	45.8	59.1	3.9	6.9	4.2	8.8	3.5	5.1	5.9	9.2
Narew	Narew	1.1	2.3	7.7	8.2	43.9	51.2	4.4	6.2	3.6	8.4	3.6	4.9	6.4	10.4
Narew	Bondary	1.2	1.6	6.4	5.5	99.2	101.1	14.6	7.5	5.3	6.2	5.9	4.1	8.9	9.5
Arithmetic mean		1.4	2.1	7.8	7.7	56.8	67.4	5.6	8.9	4.41	9.0	3.8	5.4	6.7	9.0
Standard deviation		0.29	0.07	1.13	1.17	17.83	15.23	3.33	3.9	0.67	1.67	0.98	1.72	0.85	0.93
Median		1.4	2.2	7.8	8.1	53.1	63.1	4.4	7.5	4.3	8.8	3.7	5.1	6.8	9.2

* P – Heavy metals contents in above ground parts; ** R – Heavy metals contents in roots.

Table 5

Bio-accumulation coefficientin *Carex elata* and *Acorus calamusi* in Narew River

River	Nearest locality	Bio-accumulation coefficient													
		Carex elata							*Acorus calamus*						
		Cd	Pb	Zn	Cr	Ni	Cu	Co	Cd	Pb	Zn	Cr	Ni	Cu	Co
Narew	Tykocin	1.7	0.5	1.6	0.3	0.7	0.8	4.3	0.7	0.5	1.0	0.3	0.7	0.6	3.5
Narew	Siekierki	1.2	0.5	1.9	1.0	0.7	2.8	3.3	1.3	0.6	1.8	1.1	1.0	2.5	3.5
Narew	Złotoria	1.4	0.6	2.3	0.5	0.9	2.3	3.2	1.4	0.6	1.8	0.8	1.2	3.1	2.5
Narew	Rzedziany	1.2	0.5	1.4	0.9	0.7	1.3	3.9	1.4	0.6	2.0	0.7	0.8	1.3	3.3
Narew	Bokiny	1.1	0.5	1.1	0.3	0.7	2.9	3.6	1.5	0.5	0.8	0.5	0.8	1.8	3.4
Narew	Uchowo	1.1	0.5	1.1	0.2	0.6	0.5	3.7	1.2	0.5	1.1	0.5	0.7	1.0	3.3
Narew	Doktorce	1.4	0.2	1.6	0.3	0.9	1.8	3.5	1.7	0.7	1.4	0.5	0.6	1.4	1.8
Narew	Ploski	1.2	0.5	2.4	0.6	0.8	1.2	3.0	1.6	0.6	1.7	0.6	0.8	1.6	3.5
Narew	Narew	1.4	0.6	1.5	0.4	0.7	1.6	3.5	1.6	0.6	1.1	0.5	0.7	1.5	4.4
Narew	Bondary	1.2	0.5	2.5	0.5	0.7	2.5	3.7	1.0	0.4	3.2	0.6	0.5	1.9	3.8
Arithmetic mean		1.3	0.5	1.7	0.5	0.7	1.8	3.5	1.3	0.5	1.6	0.6	0.8	1.7	3.3
Median		1.4	0.5	1.6	0.5	0.7	1.7	3.6	1.4	0.6	1.6	0.5	0.7	1.5	3.5
Standard deviation		0.29	0.057	0.52	0.24	0.09	0.82	0.36	0.29	0.09	0.70	0.22	0.19	0.70	0.71

mg · kg^{-1}. Lead is hardly mobile and hardly available to plants in bottom sediments, which was confirmed by the bioaccumulation coefficient that averaged to 0.5 (Table 5).

Zinc is an element that is essential for the proper functioning of living organisms, and its excess can be harmful. It is one of the more active metals in the environment [27]. Results of the plant material analysis indicate that there is not the issue of water environment contamination by this element. Average zinc contents in two analyzed plants of *Carex elata* and *Acorus calamus* were in the range of 38.75 ± 5.94 to 78.2 ± 12.79 mg · kg^{-1}, respectively, which according to Kabata-Pendias and Pendias [20] indicates its physiological content. The most common zinc bioaccumulation coefficient is about 1, although studies have shown its higher values: 1.7 ± 0.52 and 1.6 ± 0.70 (Table 5).

Like for zinc, there was no contamination of the environment of upper Narew River with chrome. It is generally accepted that for highly sensitive plants, Cr is harmful if present in an amount of larger than 2 mg · kg^{-1}, while medium-resistant plants tolerate content up to < 20 mg · kg^{-1} [20]. Baker and Chesnin [29] claim that concentrations above 10 mgCr · kg^{-1} in plants is excessive. Only in four samples were found excessive chromium content (one sample of *Carex elata*, 3 samples of *Acorus calamus*). The average value of bioaccumulation coefficient for Cr oscillated between 0.5 and 0.6.

Kabata-Pendias and Pendias [20] as well as Baker and Chesnin [29] report that the nickel concentration above 10 mg · kg^{-1} in the plant is excessive. All test plant samples had natural Ni content. The bioaccumulation coefficient for *Carex elata* and *Acorus calamus* varied from weak accumulation typical for nickel to moderate one. The intensive accumulation expressed above 1, was reported in a single case at *Acorus calamus*.

Copper shows a high susceptibility to bioaccumulation from the aquatic environment [27]. In a plant, this element is accumulated mainly in roots [30], as confirmed in present study. Physiological standard for copper content in plants is 5–50 mg · kg^{-1} according to Kabata-Pendias and Pendias [20] or 2–20 mg · kg^{-1} in opinion of Market [31]. The copper content in analyzed plant material ranged from 1.6 to 9.9 mg · kg^{-1} and most often it remained at a level of 3.1–6.7 mg · kg^{-1}. The range of bioaccumulation coefficient for copper was high ranging from 0.5 to 3.1.

The cobalt content in tested plants from the upper Narew River ranged 4.9 to 10.4 mg · kg^{-1} (with mean values from 6.3 ± 0.75 and 9.2 ± 0.69 mg · kg^{-1}). The toxic effects related to cobalt occur at its content range about 15–50 mg · kg^{-1}. The bioaccumulation coefficients for cobalt in *Carex elata* and *Acorus calamus* were high and amounted to 3.5 and 3.3, respectively. The results of analyzes indicate the lack of contamination due to cobalt.

Studies performed upon the chemistry at plants of two Polish lowland rivers Ołobok and Pilawa showed higher metal contents than those in the present work; mean values were: 6.2–23.0 mgPb, 255–303 mgZn, 23–55 mgCr.0, 6.6–21.4 mgNi, 12.9–78 mgCu and 4.0–23.0 mgCo · kg^{-1} [13].

Studied metals in the roots were accumulated in the following order: in *Carex elata* Zn > Co > Ni > Pb > Cr > Cu > Cd, and in *Acorus calamus* Zn > Co > Ni > Pb > Cr > Cu > Cd. In contrast, in the above ground parts, metals occurred in the following sequence: in *Carex elata* Zn > Co > Pb > Cr > Ni > Cu > Cd, and in *Acorus calamus* Zn > Pb > Co > Ni > Cr > Cu > Cd. The lowest concentrations were observed for copper and cadmium in the roots and above ground parts, while the highest ones for zinc.

Calculated bioaccumulation coefficients were as follows in roots of the examined aquatic plants: for *Carex elata* Co > Cu > Zn > Cd > Ni > Pb = Cr, and for *Acorus calamus* Co > Cu > Zn > Cd > Ni > Cr > Pb. Overall, the largest bioaccumulation coefficients in studied plants were recorded for Co and Cu, whereas the lowest for Cr and Pb. It can be also concluded that upright sedge and sweet flag in most cases accumulate examined metals in similar ways.

Studied material in the form of numerical data on metal contents was statistically analyzed. The analyses performed showed significant statistical correlations within bottom sediments between total contents of Cr and Cu and soluble forms of these elements (Table 6). It was also statistically confirmed that the Co content in *Acorus calamus* roots depends on the concentration of Co in sediments (HCl extraction). Significant correlations between the content of Pb, Zn and Cr in the roots of aquatic plants and their contents in above ground parts were recorded as well (Table 6).

Table 6

Dependencies between heavy metals contents in bottom sediments *vs* plants

Dependencies	Spearman correlation coefficient	Significance level (p)
$Cr^a - Cr^b$	0.695	$p < 0.05$
$Cu^a - Cu^b$	0.690	$p < 0.05$
$Co^{Tk} - Co^b$	0.675	$p < 0.05$
$Pb^{Tk} - Pb^{Tn}$	0.737	$p < 0.05$
$Zn^{Tk} - Zn^{Tn}$	0.951	$p < 0.05$
$Cr^{Sk} - Cr^{Tk}$	0.711	$p < 0.05$
$Cr^{Tk} - Cr^{Sn}$	0.749	$p < 0.05$

^{a} Total content in bottom sediments; ^{b} soluble forms content in bottom sediments; ^{Tk} *Acorus calamus* roots; ^{Tn} *Acorus calamus* above ground parts; ^{Sk} *Carex elata* roots; ^{Sn} *Carex elata* above ground parts.

Conclusions

1. Studies upon bottom sediments of the upper Narew River showed low contents of studied metals with an exception of cadmium. The copper content and in most cases zinc, occurred at the level of geochemical background. Lead, chromium, nickel and cobalt ranged within the 1st geochemical class, while cadmium in the 2nd class.
2. The achieved results from nickel, zinc, copper, cobalt, chromium and lead analysis in plant material indicate the lack of aquatic environment contamination with these elements; the only exception was cadmium, which exceeded the natural level.
3. It has been proven that aquatic plants are characterized by a greater tendency for metals accumulating than bottom sediments with an exception of lead and chromium.
4. It has been shown that the metal contents in most of tested plants were higher in the roots than in above ground parts.

5. Elevated cadmium content may be caused by anthropogenic activities, due to which the element passes along with the surface runoff from agricultural fields, where bad economy related to phosphorus fertilizers is run and wastewaters from sewage treatment plants; transport is also a major source of cadmium.

Acknowledgement

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MAKROFITY JAKO WSKAŹNIKI BIOPRZYSWAJALNOŚCI METALI CIĘŻKICH W GÓRNEJ NARWI

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Abstrakt: Celem przeprowadzonych badań było określenie zawartości kadmu, niklu, cynku, miedzi, kobaltu, chromu i ołowiu w osadach dennych oraz korzeniach i częściach nadziemnych roślin: *Carex elata* i *Acorus calamus* w górnej Narwi. Badania wykonano latem w 2008 r. w 10 przekrojach pomiarowych zlokalizowanych na rzece Narew (Bandary, Ploski, Doktorce, Rzędziany, Uhowo, Bokiny Złotoria, Siekierki i Tykocin). Stężenie metali oznaczano metodą ASA. Obliczone współczynniki bioakumulacji w korzeniach badanych roślin wodnych kształtowały się w następujący sposób: *Carex elata* Co > Cu > Zn > Cd > Ni > Pb = Cr i *Acorus calamus* Co > Cu > Zn > Cd > Ni > Cr > Pb. Można sądzić, że źródłem badanych metali zdeponowanych w osadach dennych i badanych roślinach wodnych w górnej Narwi jest działalność gospodarcza i bytowa człowieka, w tym wpływ lokalnej komunikacji oraz spływy powierzchniowe. Badany materiał roślinny i osady denne rzeki Narew są w niewielkim stopniu zanieczyszczone kadmem.

Słowa kluczowe: metale ciężkie, makrofity, rzeka Narew

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CHEMICAL ANALYSIS OF QUALITY OF THE DRIED SEWAGE SLUDGE AND SOLID WASTE-PRODUCTS AFTER GASIFICATION PROCESS

CHEMICZNA ANALIZA JAKOŚCI WYSUSZONYCH OSADÓW ŚCIEKOWYCH ORAZ PRODUKTÓW STAŁYCH POWSTAJĄCYCH W PROCESIE ICH ZGAZOWANIA

Abstract: This paper presents the results of chemical analysis of the quality of solid waste products (ash, char coal) obtained during gasification of dried sewage sludge. The sewage sludge originated from two different wastewater treatment systems: mechanical-biological system and mechanical-biological-chemical system with simultaneous precipitation of phosphorus. In both cases, sewage sludge was subjected to anaerobic digestion and dewatering process prior to drying. The gasification of the sewage sludge was performed in the system which is equipped with a fixed-bed reactor using air as the gasifying agent having a temperature of 298 K, and using the amount of the gasifying agent corresponding to the excess air ratio (λ) of 0.18. The ash or char coal were analyzed, among others, for the content of: alkali metals, phosphorous, sulfur, magnesium, calcium and various heavy metals. The obtained results were referred to the composition analyses of inorganic substances present in the fuel before it was subjected to the process of gasification. The influence of heat treatment on the transport of the investigated compounds was studied in the following sequence: dried sludge – gasification – solid waste. Based on the obtained results it was shown that the gasification process promotes migration of certain substances such as zinc or phosphorus from the sludge into the solid phase formed after the heat treatment of the sludge. The potential for further use of the solid by-products generated during the gasification of sewage sludge was presented in the conclusions of the study.

Keywords: sewage sludge, gasification, solid waste products, inorganic compounds

Gasification is considered to be a promising method for the disposal of sewage sludge. This process, apart from a valuable gas fuel, generates solid and liquid waste

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by-products. The former are generated as a result of the transition of the mineral substance into the solid phase [1–4]. Those solid by-products are primarily ashes, and in special cases also char coal [2]. The formation of char depends on the composition of non-combustible inorganic substances in the sludge resulting in a significant reduction in the characteristic temperatures of ash [5]. Liquid waste products, such as tars, are generated as a result of condensation of the impurities present in the gas.

The parameters of the process the gas produced during gasification of sewage sludges were previously discussed by the authors of the this paper in [5, 6]. The gas produced by the gasification of the sewage sludges originating from various wastewater treatment systems was analysed for the volume fraction of nitrogen, oxygen, carbon monoxide, hydrogen, carbon dioxide and methane. It was determined that the volume fraction of the main combustible components of the gas, i.e. carbon monoxide and hydrogen is greater in the case of the gasification of the sewage sludge which originated from the mechanical-biological wastewater treatment plant operating in the mechanical-biological system as compared to the sludge from the mechanical-biological-chemical wastewater treatment system with a simultaneous precipitation of phosphorus. It was also shown that the parameters of the process gas depend on the process conditions. The most important factors include the amount and temperature of the gasifying agent.

Sewage sludge, apart from energetically favourable compounds, is the source of toxic and hazardous organic and inorganic contaminants. Organic compounds identified in it include [7–10]: dioxins and furans, polychlorinated biphenyls, chlooroorganic pesticides, adsorbed and extracted chloro derivatives, polycyclic aromatic hydrocarbons, phenols and their derivatives, phthalates, sex hormones and others. The group of hazardous inorganic compounds assayed in sewage sludge contains primarily various heavy metals occurring over wide ranges (mg/kg d.m. for raw sewage) [11–17]: arsenic 3–230, cadmium 1–3410, chromium 10–990000, copper 80–2300, nickel 2–179, lead 13–465, zinc 101–49000. Based on this information it can be assumed that sewage sludge gasification by-products can be also contain mentioned above toxic and harmful substances.

The preliminary research [18] found that the toxic effect of the products produced during sewage sludge gasification depends on both the type of a sample tested (ash, char coal, tar) and sewage sludge used. The research was carried out, using a Microtox® test with *Vibrio fisheri* bacterial strain (luminescence method). Higher toxicity was found in the samples of ash that formed during gasification of sewage sludge, which appeared to be more toxic, than for the sludge of lower toxicity. As for the tar samples, they were all toxic regardless of the sludge gasified. Thus, from the cognitive perspective, the characteristics of such samples in terms of different contaminants which might be responsible for their toxicity are significant.

This paper presents the results of the comparative chemical analysis of the quality of dried sewage sludges and solid waste products (ash, char coal) obtained during the gasification of dried sewage sludge. The investigation of the transport of inorganic substances (alkali metals, phosphorus, sulfur, magnesium, calcium and various heavy metals) in the following sequence: dried sewage sludge – gasification – solid waste, is important both for the assessment of the ecological risks and the potential for their further application (valorization and recovery).

Materials and methods

Two different sewage sludges, which were selected for the study, originated from wastewater treatment plants situated in Poland. Sewage sludge 1 originated from a wastewater treatment plant operated as a mechanical-biological system, and sewage sludge 2 originated from a mechanical-biological-chemical wastewater treatment system with simultaneous phosphorus precipitation. The sludges generated in the wastewater treatment plants are subjected to anaerobic digestion and next after dewatering are dried in a cylindrical dryer on the shelves heated to 533 K (sewage sludge 1) and using hot air of a temperature of 423 K in a belt dryer (sewage sludge 2). In the end, the resulting sewage sludge 1 was in the form of granulate, and sewage sludge 2 was in the form of irregularly cut "noodles" (Fig. 1).

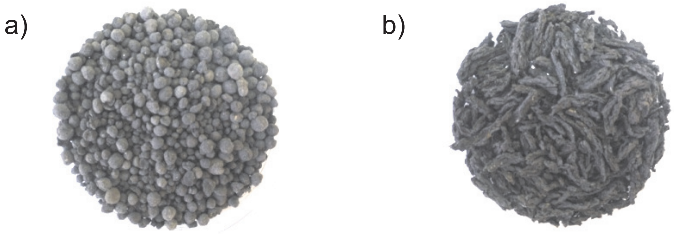

Fig. 1. Sewage sludge analyzed: a) No. 1; b) No. 2

The studied sewage sludges were gasified in the system equipped with a fixed-bed reactor (Fig. 2) using air as the gasifying agent having a temperature of 298 K, and using the amount of the gasifying agent corresponding to the excess air ratio (λ) of 0.18. The applied gasifier was designed as a counter-current system operated under low overpressure generated by an air forced-draught fan. The main element of the installation is the gasification reactor with an inner diameter of d_w = 150 mm and a total height of H = 250 mm. The maximum mass of the feedstock consisting of the dried sewage sludge is m_{pal} = 5 kg. The sewage sludge is introduced into to the reactor from the sludge tank through the top of the reactor. The gasifying agent is introduced through the bottom of the reactor. The fuel moves through the reactor in a countercurrent direction and through the successive zones: drying, pyrolysis, reduction and combustion. The moisture is evaporated in the drying zone. In the pyrolysis zone, the sludge is subjected to thermal conversion into the volatile fractions and the solid form. In the reduction zone, carbon is transformed and carbon monoxide and hydrogen are produced. Those compounds are the main components of the combustible gas produced in the gasification process. Combustion of the remaining solid part occurs in the combustion zone leading to heat production. The produced heat is then used in endothermic reactions occurring in the upper zones. The gasification reactor does not have an automatic fuel feeding system, however, it is not a type of sequencing batch reactor type (termed as 'batch reactor') in which a single batch of fuel is gasified from start to finish. During the measurements, the reactor was fed by an additional amount of

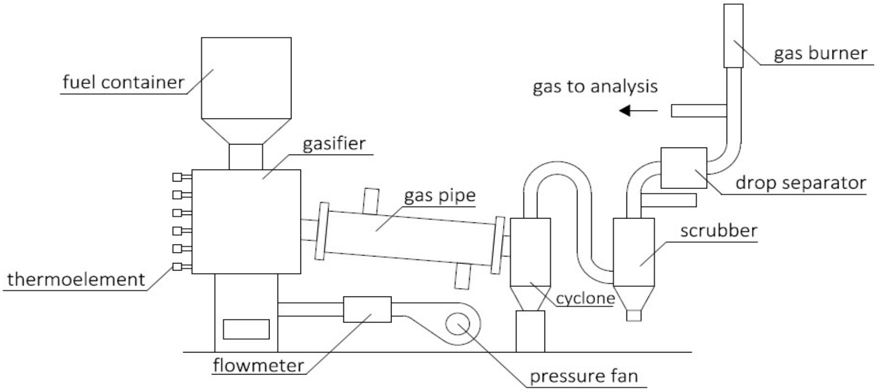

Fig. 2. Fixed bed installation

fuel by ejection of successive baffles located in the fuel tank. This was aimed to maintain the operating conditions, which would be similar to the conditions occurring in the industrial installation. The rate of fuel gasification allowed for manual addition of a specified amount of granulates/noodles, which occurred periodically when the air supply was stopped. This temporary suspension of the air supply was not found to significantly lower the internal temperature of the gasifier. After refueling, and reintroducing the air, the gasifier was restarted. The observed decrease in the internal temperature of the reactor was mainly caused by the imbalance of the system upon the addition of the fuel.

The effect of the gasification parameters on producer gas yield, its composition and calorific value in particular, are discussed in detail in [5, 6]. As far as the by-products are concerned (Fig. 3), the gasification of sewage sludge 1 produced both ash (taken from the ash-pan) and char coal (taken from the inside of the reactor), while sewage sludge 2 produced ash only. Char coal existing in the case of sewage sludge number 1 was caused by the composition of the inorganic, non combustible substance in sewage sludge which can decrease fusion temperatures of ash [5].

Chemical analysis of the quality of the dried sewage sludge and the solid products formed in the process of gasification included an assessment of the content of the primary elements (carbon, hydrogen, nitrogen, chlorine, fluorine, sulfur, and oxygen), alkali

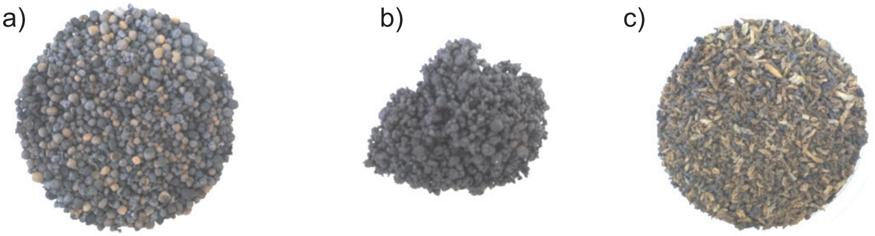

Fig. 3. By-products of sewage sludge gasification: a) ash and b) char coal from sewage sludge no 1 and ash c) from sewage sludge 2

metals, phosphorus, magnesium and calcium (mineral elements) as well as selected heavy metals. The content of the primary elements was determined automatically by IR analyzer. On the other hand, the content of mineral elements and heavy metals in the test samples was determined by means of absorption or plasma spectrometry.

In the previous studies the following parameters of the sewage sludges subjected to the gasification were determined: moisture content, volatile substances and ash content, heat of combustion and calorific value. The content of moisture, volatile substances and ash were determined by gravimetric method described in these standards: PN-EN 14774-3:2010, EN 15402:2011 and EN 15403:2011, respectively. In contrast, the heat of combustion was determined by calorimetric method, and the calorific value was calculated using the mass fractions of the main elements in the sample. The determined sludge properties are shown in Table 1

Table 1

Sewage sludge properties

Analysis and test feature		Sewage sludge	
		No 1	No 2
Proximate analysis, [%] (as received)*	Moisture	5.30	5.30
	Volatile matter	51.00	49.00
	Ash	36.50	44.20
Ultimate analysis, [% d.m.]	C	31.79	27.72
	Cl	0.22	0.03
	F	0.013	0.003
	H	4.36	3.81
	N	4.88	3.59
	O (by difference)	20.57	18.84
	S	1.67	1.81
Mineral components contents, [% d.m.]	Ca	10.87	16.02
	K	1.34	0.77
	Mg	2.10	1.37
	Na	0.56	0.73
	P	9.07	6.19
Heavy metal contents, [mg/kg d.m.]	As	4.19	3.94
	Cd	6.47	3.24
	Cr	180.53	584.53
	Cu	495.30	183.16
	Hg	0.99	0.96
	Ni	103.67	18.90
	Pb	119.30	59.97
	Se	9.84	1.70
	Zn	920.90	991.20
Calorific value [d.m.]*	HHV, MJ/kg	14.05	11.71
	LHV, MJ/kg	12.96	10.75

* Based on the works [5, 6].

Results and discussion

The comparison of the tested sewage sludges allow for conclusion that sewage sludge 1 has higher calorific value than sewage sludge 2 (Table 1). This was confirmed by the study of gas composition and its calorific value presented in [5–7]. The primary contamination of the tested sewage sludges by inorganic substances varied in terms of mass fraction of individual elements, including heavy metals (Table 1, Fig. 4 and 5). For example, the content of three (potassium, magnesium, phosphorus) of the five tested mineral elements (calcium, potassium, magnesium, sodium, phosphorus) was higher in sewage sludge 1 than in sewage sludge 2. Also, in the case of heavy metals, it was observed that the content of seven (arsenic, cadmium, copper, mercury, nickel, lead, selenium) of the nine analyzed heavy metals (arsenic, cadmium, chromium, copper, mercury, nickel, lead, selenium, zinc) was higher in sewage sludge 1 than in sewage sludge 2. The total content of heavy metals in the sewage sludges was, however, similar and was equal to 1841 mg/kg d.m. for sewage sludge 1 and 1848 mg/kg d.m. for sewage sludge 2. It is noteworthy that sewage sludge 2 had 3-fold higher chromium concentration as compared to sewage sludge 1, which could cause its toxicity. This phenomenon was described previously in [18].

As it was mentioned above, two types of solid by-products are produced in the case of the gasification process for sewage sludge 1, this is, ash and char coal. Based on the results of chemical analysis it was determined that the mass fraction of phosphorus and calcium in the generated solid products was greater than for the sewage sludge sample prior to the heat treatment, with the greatest accumulation observed in the char samples (Fig. 4a). A similar trend was observed in the case of sewage sludge 2 and the ash produced during gasification of this sludge (Fig. 4b). Similar effects are given in paper [19] which points out that phosphorus concentration in the ash formed after sewage

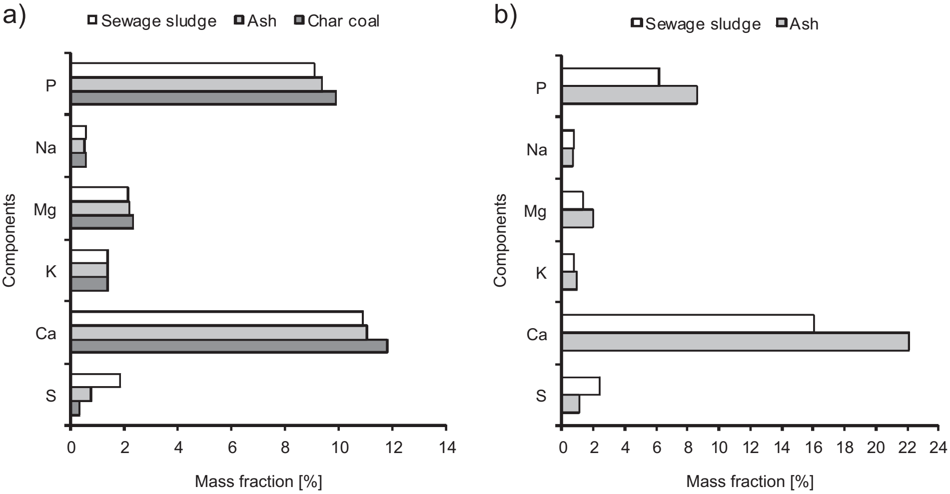

Fig. 4. Mass fraction of the selected components in sewage sludge a) No. 1; b) No. 2 and in solid waste gasification products

sludge gasification increased from 14.1 mg/kg d.m. to 20.6 mg/kg d.m. (an increase by 68 %).

Also in the case of heavy metals it was shown that their concentration was higher in the ash and char coal samples than in the sludge samples (Fig. 5a–d). This observation was valid for seven (arsenic, cadmium, copper, mercury, nickel, lead, selenium) of the nine analyzed heavy metals (arsenic, cadmium, chromium, copper, mercury, nickel, lead , selenium, zinc) regardless of the type of sewage sludge. Similar conclusions were drawn by the authors of paper [12] who found an increase in the concentrations of

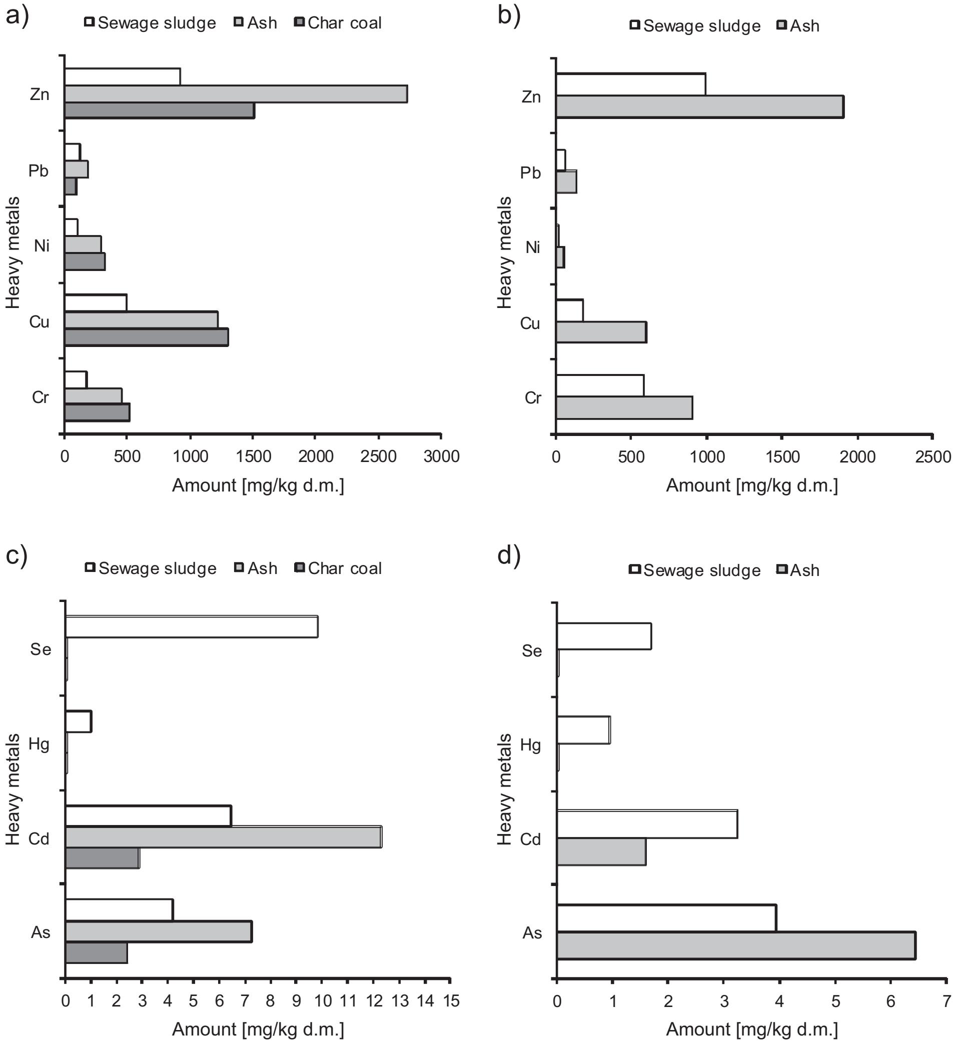

Fig. 5. Amount of the selected heavy metals in sewage sludge and in solid waste gasification products (no 1 – a and c, no 2 – b and d)

cadmium (from 0.93 to 1.67 mg/kg d.m.), chromium (from 80.82 to 247.95 mg/kg d.m.), copper (from 580.36 to 922.14 mg/kg d.m.), lead (from 78.27 to 125.09 mg/kg d.m.) and zinc (from 402.09 to 637.50 mg/kg d.m.) in sewage sludge and ash samples after gasification. The difference was observed, however, in the extent of accumulation of the heavy metals in the solid products. For example, in the case of the zinc concentration in the samples of the ash generated in the gasification process it was observed that it increased 2-fold for sewage sludge 2, and 3-fold for sewage sludge 1.

The presence of heavy metals in solid products generated during the gasification of sewage sludge has a potential impact on their use or disposal. It is commonly known that one of the main obstacles to agricultural use of sewage sludge is the high content of heavy metals, which can be transferred from sludge to the soil environment causing pollution [15]. This rule will also apply to the feasibility assessment of the application of sewage sludge gasification by-products. Taking into consideration the increase of the concentration of heavy metals in solid products formed during the gasification of sewage sludge, which was evidenced by the presented results, it should be noted that there is an ecological risk associated with this type of waste. It is mainly due to the presence of chromium. This was confirmed by the results of toxicity tests for these samples, which were presented in previous studies [18].

The analysis of heavy metals contamination of by-products and sewage sludges subjected to gasification allows for assumption that the generated process gas will be only slightly contaminated by these substances. Most of the inorganic substances initially present in the sludge gasified in a fixed-bed reactor accumulate in the solid by-products generated during the process. For this reason, the sewage sludge gasification technology (implemented in a fixed-bed reactor) is competitive with other methods used for this purpose. Because of that, for example, during combustion of sewage sludge in a fluidized bed boiler a higher concentration of heavy metal is observed in the fly ash than in the so-called bottom ash [20], which consequently causes the possibility of the emission of these pollutants into the environment.

The authors suggest that further research should concentrate on the recovery of phosphorus from solid products (ash and char coal) formed during the gasification of sewage sludge e.g. through leaching phosphorus from ash or sinter with mineral acids. The application of ash resulting from gasification to the sorption of toxic and hazardous compounds (e.g. heavy metals) from different sewage is also worth considering. Similar research has already been carried out, using dried sewage sludge [21, 22].

Conclusion

Based on the results of the study it was shown that the gasification process promotes migration of certain inorganic compounds, such as zinc or phosphorus from the sludge into the solid phase formed after the heat treatment of the sludge. This phenomenon depended both on the type of solid by-product (ash, char) and the used sludge. Taking this into consideration, the future research direction is to study the recovery of phosphorus from solid products generated during the gasification of sewage sludge, for example, by leaching of phosphorus from the ash or char by mineral acids. On the other hand, this study evidenced large accumulation of heavy metals, mainly chromium, in the analyzed solid by-products. This indicates the ecological threat posed by this type of waste, which can potentially be toxic. However, it can be attempted to use the gasification ash for the sorption process of toxic and hazardous compounds (e.g. heavy metals) from various kinds of wastewater.

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CHEMICZNA ANALIZA JAKOŚCI WYSUSZONYCH OSADÓW ŚCIEKOWYCH ORAZ PRODUKTÓW STAŁYCH POWSTAJĄCYCH W PROCESIE ICH ZGAZOWANIA

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Abstrakt: W pracy przedstawiono wyniki analiz chemicznych jakości stałych produktów odpadowych (popiół, spiek) uzyskanych podczas zgazowania wysuszonych osadów ściekowych. Osady ściekowe pochodziły z dwóch różnych układów oczyszczania ścieków, tj. mechaniczno-biologiczny i mechaniczno-biologiczno-chemiczny z symultanicznym strącaniem fosforu. W obu przypadkach przed procesem suszenia osady ściekowe poddawano fermentacji i odwodnieniu. Proces zgazowania osadów ściekowych prowadzono w instalacji wyposażonej w reaktor ze złożem stałym przy użyciu powietrza jako czynnika zgazowującego o temperaturze 298 K oraz stosując ilość czynnika odpowiadająca stosunkowi nadmiaru powietrza (λ) 0,18. Analiza obejmowała ocenę zawartości w popiele, czy też spieku m.in. metali alkalicznych, fosforu, siarki, magnezu, wapnia, a także różnych metali ciężkich. Otrzymane wyniki odniesiono do analiz składu substancji nieorganicznej występującej w paliwie przed poddaniem go procesowi zgazowania. Przeanalizowano wpływ obróbki termicznej na transport badanych związków na drodze: wysuszony osad ściekowy – proces zgazowania – stały produkt odpadowy. Na podstawie wyników badań wykazano, że proces zgazowania promuje migrację niektórych związków, jak na przykład fosforu czy też cynku z osadu ściekowego do fazy stałej powstałej po obróbce termicznej tego osadu. We wnioskach pracy przedstawiono również potencjalne możliwości dalszego wykorzystania stałych produktów ubocznych powstających podczas zgazowania osadów ściekowych.

Słowa kluczowe: osady ściekowe, zgazowanie, stałe produkty uboczne, związki nieorganiczne

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Anna JANICKA[1]

CAR CABIN ATMOSPHERE QUATILTY: VEHICLE INTERIOR TOXICITY ASSESMENT BASED ON *IN VITRO* TESTS

JAKOŚĆ POWIETRZA WE WNĘTRZU KABINY SAMOCHODU: OCENA TOKSYCZNOŚCI WNĘTRZA POJAZDU BAZUJĄCA NA TESTACH *IN VITRO*

Abstract: In the article the problem of vehicle interior as an important environment of human life hase been discussed. The problem is very important in aspect of indoor air quality. A vehicle interior is a specific environment where levels of volatile toxic organic compounds concentrations are particularly high.

In the article the results of statistical analysis of human resistance time in vehicle interior are presented. A method of gaseous mixtures toxicity estimation based on *in vitro* tests has been proposed in application for vehicle cabin interior and compared to the popular toxicity indicators (relative toxicity coefficients). The results of the method application in brand new passenger vehicles (in parking conditions) are presented. The results was correlated with volatile organic compounds concentration in vehicles interior (method: gas chromatography).

Keywords: vehicle interior, volatile organic compounds, indoor measurements, toxicity

Introduction

Vehicle cabin contributes specific environment of human existence where the level of volatile organic compounds (VOCs) concentration in air can be even few times higher than outside [1, 2]. To emphasis the mining of vehicle interior as an important issue of public health sector the statistic research has been prepared. According to respondents answers in Wroclaw city, average time spent inside passenger vehicle is 1 hour and 20 minutes per day (Fig. 1) and 27 minutes in public transport vehicles (Fig. 2).

The main exposure route of those substances is inhalation, which accounts for 99 % of the total exposure of the general population. The health effects of toxic volatile

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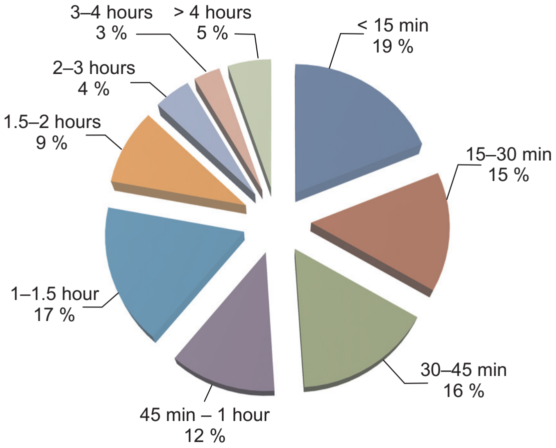

Fig. 1. Time spent in passenger vehicles (own research based on Wroclaw citizens)

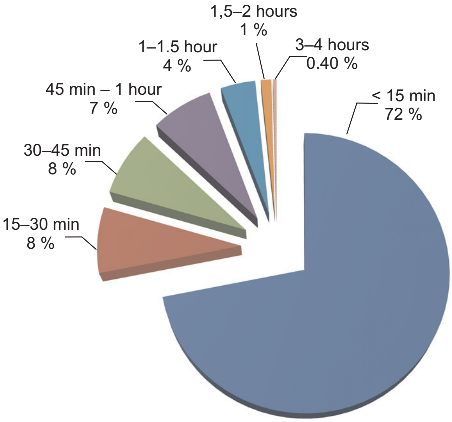

Fig. 2. Time spent in public transport vehicles (own research based on Wroclaw citizens)

compounds are well documented: acute (short-term) inhalation exposure of humans to benzene may cause drowsiness, dizziness, headaches, as well as eye, skin, and respiratory tract irritation, and, at high levels, unconsciousness. Chronic (long-term) inhalation exposure has caused various disorders in the blood, including reduced numbers of red blood cells, aplastic anemia, and even leukemia [1].

The methods of investigation of substance toxic activity can be general divided on [2]:

– estimation of substance toxicity based on relation between chemical structure of substance and its biological activity (new direction of toxicology science),

– investigation of substance toxicity based on tests on animals (the most popular method),

– alternative methods based on rule 3R (replacement, reduction, refinement) which aim is to eliminate or reduce of animal suffer.

For toxicity estimation and analysis of the group of substances usually data for one representative and common compound occurring in environment are used (*ie* benzene for VOCs group). The intensity of mutagenic, carcinogenic, irritant or sensitize activity of other compounds from the group is counted in relation to the representative compound. This method can be used to determine Relative Toxicity (mutagenic, carcinogenic, irritant or sensitize) Coefficient (RTC) for all substances from the group. Because of discussible, law-based toxicity equivalent factors or relevant toxicity coefficients measures of mixtures toxicity the direct methods of toxicity estimation are needed to be developed [3]. The example is an *in vitro* method which has been proposed and developed by the article author [4, 5].

Methodology

The indoor air samples was up-taken from two new (month after manufacture date) different brands vehicles interior: Japanize (vehicle A) and German (vehicle B) production, same class, similar equipment.

The samples of inner air were uptaken by active coal tubes (for chromatography) and based on the ISO/DIS 12219-1draft international standard [6] by special flasks with human lung cells previously prepared in Institute of Immunology and Experimental Therapy of Polish Academy of Science laboratories.

The sampler was put into popular, brand new, passenger-vehicle interior and plugged-in to aspirator (ASP II) the localization of system inlet is presented on Fig. 3 and exposed for 4 hours.

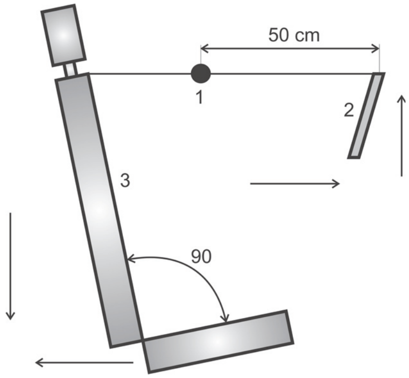

Fig. 3. Schematic arrangement of the sampling position in test vehicle: 1 – sampling point; 2 – steering wheel; 3 – seat with head rest

After sampling procedure the samplers consist standardized cell-culture system (human cell line A549 was analyzed). Cell growth, cell morphology and cell viability were used as parameters to determine the cytotoxicity of vehicle interior atmosphere. The measure the lethality effect on cells was determined spectrophotometrically with the use of a mitochondrial enzyme activity assay for mitochondrial succinct dehydrogenase activity by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT assay).

The A549 cells are maintained in Dulbecco's modified Eagle's minimum essential medium (DMEM), and the L929 cells were kept in Eagle's supplemented with 10 % calf serum (c.s), 2 mM L-glutamine, antibiotics (100 U/cm^3 penicillin and 100 1 g/cm^3 streptomycin).

According to Polish standard (PN-EN ISO 10993-5) cytotoxicity is investigated on two cells lines. Measuring in vitro growth of mouse fibroblast L929 and human A549 cell line.

For cytotoxicity test, the cells are seeded in the 24-well plates (Nunc) of 1 cm^3 at density of 2×105 cells/cm^3 in the culture medium Eagle'a or DMEM with 2 % calf serum, penicillin and streptomycin is deposited into each well. Samples of the tested samples contain VOCs are added to prepared cells, which are then incubated for 24 h, 48 h and 72 h at 37 ^{o}C in the atmosphere of 5 % CO_2 in air.

VOC's samples were up taken by tubes with active coal (SKC lot 2000). The analysis was done according to Polish standard: PN-EN ISO 16017-1: 2006. The qualitative and quantitative analysis was proceed on Varian 450 GC gas chromatograph with FID detector and capillary column was used for quantity and quality analysis. Carbone disulfide (CS_2) was used for VOCs extraction from active coal. The chromatography conditions were: column temperature (110 ^{o}C), dozers (150 ^{o}C) and detectors (250 ^{o}C).

Relative Toxicity Coefficients were calculated for most characteristic in-vehicle compounds and VOCs group based on to two Polish standards of Maximum Allowed Concentrations: for indoor environment and for workplaces according to the Table 1.

Table 1

Relative Toxicity Coefficients (RTC) for chosen compounds and VOCs groups

Chemicals name	Indoor Maximum Allowed Concentration (spaces A category) (IMAC) [8] [μg/m^3]	RTC according to IMAC (RTC-IMAC)	Maximum Allowed Concentration for Workplaces (MACW) [7] [mg/m^3]	RTC according to MACW (RTC-MACW)
Toluene	200	0.05	100	0.016
Benzene	10	1	1.6	1
Ethylbenzene	100	0.1	100	0.016
Xylene (isomers)	100	0.1	100	0.016
Groups				
Aromatic HC	66	0.15	49	0.033
Alifatic HC	250	0.04	678	0.002
Other VOCs	90	0.11	170	0.009
Total VOCs	135	0.07	229	0.007

Results

The results was presented in tables and figures.

In Table 2 the results of *in vitro* tests toxicity are presented as number of dead cells after 72 hours of cultivation after exposition on vehicle interior atmosphere and number of cells in control sample to number of exposed cells (α) after 72 h.

Table 2

In vitro testes results

Sample description	New vehicle 1 (brand A)			New vehicle 2 (brand B)		
	Number of cells, N (72 h)	$\alpha = N_i/N_{control}$	Dead cells [%]	Number of cells, N (72 h)	$\alpha = N_i/N_{control}$	Dead cells [%]
Control sample	94 000 000	1.00	0	240 000 000	1.00	0
Interior 1	40 000 000	2.35	2	8 000 000	30.00	26
Interior 2	32 000 000	2.94	10	3 200 000	75.00	75
Interior 3	38 000 000	2.47	6	4 500 000	53.33	50
Interior average	37 000 000	2.56	6	5 200 000	45.86	50
Background	81 000 000	1.16	0	190 000 000	1.26	0

In Fig. 4 the comparison of the *in vitro* tests results for both vehicles interiors is presented.

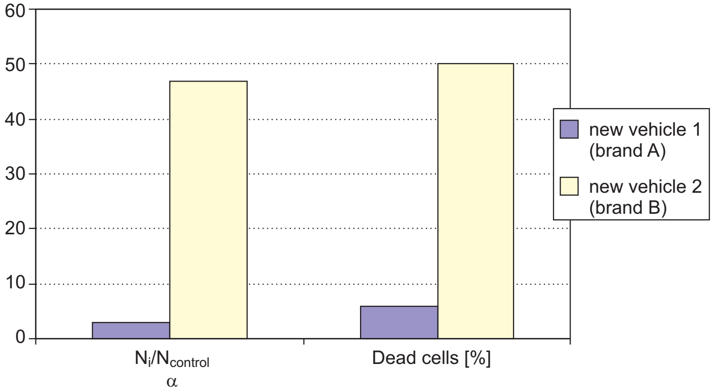

Fig. 4. Comparison of the *in vitro* tests results for both vehicles interiors

In vitro tests indicates that interior of vehicle 2 is almost 10 times more toxic than vehicle 2 for human lung cells. The atmosphere inside second vehicle cabin after 4 hours direct exposition caused lethal effect for half cell line and inhibits cell growth in almost 50 % in comparison to control sample. In case of vehicle no. 1 the exposition caused dead of 6 % of the culture and almost 3 % inhibition of human lung cell line growth.

In Table 3 the results of chromatographic analysis an computational results of toxicity indicators are presented.

Table 3

Relative Toxicity Coefficients for chosen compounds and VOCs groups

Compound	New vehicle 1 (brand A)			New vehicle 2 (brand B)		
	Average concentration (C_i) [μg/m^3]	RTC-IMAC	RTC-MACW	Average concentration (C_i) [μg/m^3]	RTC-IMAC	RTC MACW
Toluene	29.5	1.5	0.5	249.2	12.5	4.0
Benzene	39.3	39.3	39.3	114.8	114.8	114.8
Ethylbenzene	8.4	0.8	0.1	411.3	41.1	6.6
Xylene (isomers)	17.3	1.7	0.3	26.5	2.6	0.4
Groups						
Aromatic HC	188.7	28.8	6.2	608.4	92.8	19.8
Aliphatic HC	1303.1	52.1	3.1	507.8	20.3	1.2
Other VOCs	185.4	20.6	1.7	275.8	30.6	2.6
Total VOCs	1677.2	124.1	11.7	1641.2	121.4	11.4

In Figs 5 to 7 the concentrations of VOCs groups and Relative Toxicity Coefficient (RTC) according to IMAC and MACW are compared for both vehicles.

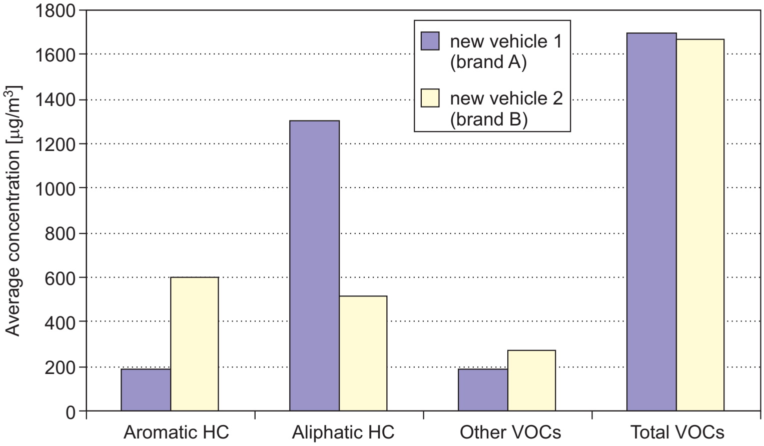

Fig. 5. Average concentration of VOCs groups in cabin air [μg/m^3]

The difference between total VOCs concentrations in both vehicle is insignificant. The differences in VOCs group share are visible. In case of vehicle no. 2 concentration of aromatic hydrocarbons is two times higher than in vehicle 2 interior atmosphere.

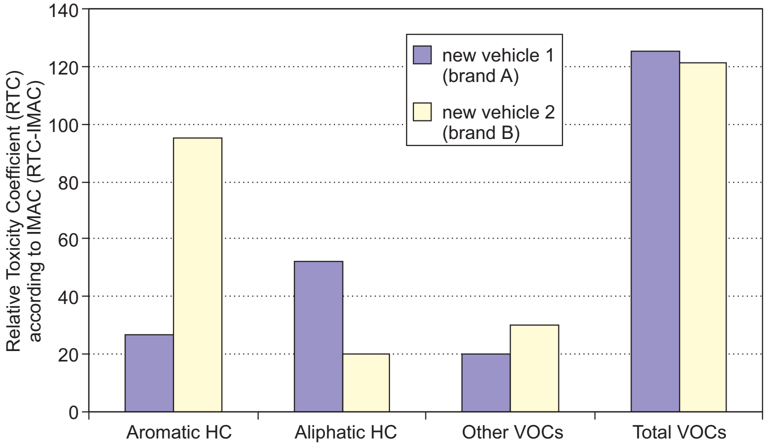

Fig. 6. Relative Toxicity Coefficient (RTC) according to IMAC

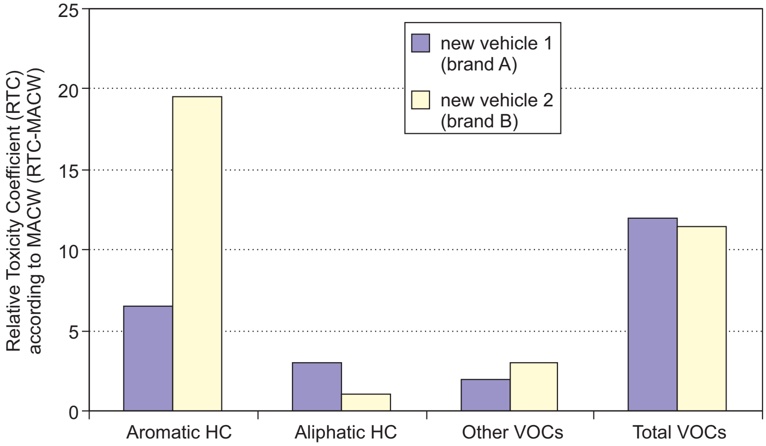

Fig. 7. Relative Toxicity Coefficient (RTC) according to IMAC

The computational toxicity indictors show the significant differences between using different bases of calculation methods (MAC for indoor atmosphere and MAC for workplaces).

Conclusions

Gaseous mixtures toxicity is complex and complicated problem for evaluation. Because of discussible, law-based computational toxicity indicators measures of mixtures toxicity the direct methods of toxicity estimation are needed to be developed. The example is the method which has been proposed and developed by the article author. Despite the fact that the total VOCs concentration is almost the same in cabin of both cars, proposed by the author *in vitro* tests on human lung cells indicates that interiors of two new vehicles (month after manufacture date), same class, similar equipment can be 10 times more toxic. It also proof that RTC methods need to be evaluated. The RTC calculations based on two different standards shows that the method is discussable but proofed toxicity determined effect for aromatic hydrocarbons. Compared to the *in vitro* tests it shows that very complicated effects of synergism can strongly impact on real toxic effect of volatile toxins on human respiratory system.

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JAKOŚĆ POWIETRZA WE WNĘTRZU KABINY SAMOCHODU: OCENA TOKSYCZNOŚCI WNĘTRZA POJAZDU BAZUJĄCA NA TESTACH *IN VITRO*

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Politechnika Wrocławska

Abstrakt: W artykule podjęto dyskusję nad trudnym problemem oceny toksyczności mieszanin gazowych. Problem jest istotny szczególnie w aspekcie jakości powietrza w środowisku przebywania człowieka a w szczególności w pomieszczeniach zamkniętych. Takim środowiskiem jest wnętrze kabiny pojazdu, w którym stężenia związków toksycznych są szczególnie wysokie.

W artykule przedstawiono wyniki badań statystycznych dotyczące czasu przebywania człowieka we wnętrzu pojazdów. Zaprezentowano metodę oceny toksyczności mieszanin gazowych opartą o badania *in vitro* oraz możliwości jej aplikacji w kabinach pojazdów. Przedstawiono również wyniki badań mających na celu ocenę toksykologiczną wnętrza różnego typu nowych pojazdów samochodowych w warunkach parkingowych. Wyniki badań zestawiono z pomiarem stężeń lotnych związków organicznych (metoda chromatografii gazowej z detekcją mas).

Słowa kluczowe: wnętrze pojazdu, lotne związki organiczne, pomiary jakości powietrza wewnętrznego, toksyczność

Varia

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Jan KŘÍŽ – University of Hradec Králové, Hradec Králové, CZ
Tadeusz MAJCHERCZYK – Opole University, Opole
Małgorzata RAJFUR – Opole University, Opole
Aleksander ZAREMBA – Czestochowa University of Technology, Częstochowa
Zbigniew ZIEMBIK – Opole University, Opole

SPONSOR of the ECOpole '13 Conference
Ministry of Science and Higher Education, Warszawa

Invited speakers of ECOpole'13 Conference

	Miroslav ČERNÍK (Technical University of Liberec, Liberec, CZ)	*Technologies for groundwater remediation based on application of zero-valent iron nanoparticles*
	Marina V. FRONTASYEVA (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, RU)	*Contribution of the Joint Institute for Nuclear Research to the programme of the United Nations on the study of atmospheric deposition of heavy metals in Europe based on moss analysis*
	Władysław KAMIŃSKI and Elwira TOMCZAK (Lodz University of Technology, Łódź, PL)	*Low-cost sorbents applications for water treatment*
	Jacek NAMIEŚNIK, Łukasz MARCINKOWSKI and Adam KLOSKOWSKI (Gdansk University of Technology, Gdańsk, PL)	*Green aspects of sample preparation techniques for isolation of organic analytes from environmental samples*
	Eiliv STEINNES (Norwegian University of Science and Technology, Trondheim, NO)	*Metal contamination of the terrestrial environment from long-range atmospheric transport: evidence from 35 years of research in Norway*

Short Conference Report

The Conference ECOpole '13 was held in 23–26 X 2013 in Hotel Ziemowit in Jarnoltowek, PL. It was the twenty second ecological conference of the series of meetings organised by the Society of Ecological Chemistry and Engineering, Opole, PL.

133 participants, including delegates representing following countries: Czech Republic, Germany, Great Britain, Norway, Poland, Russian Federation, took part in the event and presented 23 oral contributions and 124 posters.

The Abstracts of the Conference contributions were and are available on the Conference website

ecopole.uni.opole.pl

The Conference issue of the quarterly *Ecological Chemistry and Engineering S* containing among others keynote speakers papers, was distributed at the Conference Reception desk together with a CD-ROM (containing short info on Keynote Speakers, Abstracts of the Conference presentations as well as ECOpole '13 Conference Programme).

On Wednesday (23rd October 2013) at 19.00 after a brief Opening Ceremony performed by prof. Maria Wacławek Chairperson of the Organising Committee and prof. Witold Wacławek, Chairman of the Conference Scientific Board and President of the Society of Ecological Chemistry and Engineering, the participants were invited for the Guitar recital of Tadeusz Pabisiak entitled: *From Bach to Beatles*. The Programme contained works by J.S. Bach, I. Albeniz, F. Chopin, P. de Lucia, V. Gomez, E. Lecuona, N. Paganini, and also J. Lennon and P. McCartney. The audience applauded the player and claimed for encore.

The Conference Agenda was divided into 4 sections:

- SI Ecological Chemistry and Engineering
- SII Environment Friendly Production and Use of Energy
- SIII Forum of Young Scientists and Environmental Education
- SIV Health, Ecology and Agriculture.

On Thursday, 24th October 2013 at 9.00 a.m. prof. Eiliv STEINNES (Norwegian University of Science and Technology, Trondheim, NO) initiated the First Plenary Session with the invited lecture: *Metal contamination of the terrestrial environment from long-range atmospheric transport: evidence from 35 years of research in Norway.* Then was delivered a lecture of authors prof. Jacek NAMIEŚNIK, Łukasz MARCINKOWSKI and Adam KLOSKOWSKI (Gdansk University of Technology, Gdańsk, PL): *Green aspects of sample preparation techniques for isolation of organic analytes from environmental samples*. During the conference the plenary lectures were also delivered by other invited lecturers: prof. Marina V. FRONTASYEVA (Joint Institute for Nuclear Research, Dubna, RU): *Contribution of the Joint Institute for Nuclear Research to the programme of the United Nations on the study of atmospheric deposition of heavy metals in Europe based on moss analysis*, prof. Miroslav ČERNÍK (Technical University of Liberec, Liberec, CZ): *Technologies for groundwater remediation based on application of zero-valent iron nanoparticles* and prof. Władysław KAMIŃSKI and Elwira TOMCZAK (Lodz University of Technology, Łódź, PL): *Low-cost sorbents applications for water treatment.*

There were also presented very interesting lectures, *eg* by dr Z.A. SZYDŁO (Highgate School, London, UK): *The chemical theatre – education, enlightenment, entertainment* – this contribution was met with great interest of the audience, prof. S. FRÄNZLE and A. BAUER (Internatinal School Zittau (IHI), DE): *Biomonitoring and ore prospection by means of chitin and living arthropods*, S.V. GORELOVA, M.V. FRONTASYEVA, A.V. GORBUNOV, S.M. LYAPUNOV and O.I. OKINA (L.N. Tolstoy TSPU, Tula, RU): *Exotic woody shrubs which can be used for bioaccumulation of technogenic pollution in urban ecosystems of non-chernozem zone of Russia*, E. TOMCZAK and A. DOMINIAK (Lodz University of Technology, Łódź, PL): *Historical changes in the water supply system and maintenance of drinking water quality standards in the city of Lodz*, T. OLSZOWSKI

(Opole University of Technology, Opole, PL): *Study of scavenging PM_{10} by large-scale precipitation* (*frontal rainfall*) and T. CIESIELCZUK and C. ROSIK-DULEWSKA (Opole University, Opole): *Possibility of compost use as a sorbent of petroleum products in simulated conditions*.

Thursday, a day of hard work, was finished with the Poster Session. Many of the discussions started at the posters, lasted until the evening hours.

At 19.30 the Conference participants were invited for a Conference Dinner.

As usually during the ECOpole Conferences, the second day included the Session of the Young Scientists (a forum of young scientists that present and discuss local ecological problems of their countries). During the Young Scientists' and Environmental Education Poster Session 35 posters were presented.

The Scientific Board: prof. Maria WACŁAWEK (Opole University, Opole, PL) – Chairperson, prof. Marina V. FRONTASYEVA (Joint Institute for Nuclear Research, Dubna, RU), prof. Stefan FRÄNZLE (IHI, Zittau, DE), prof. Bohumil VYBÍRAL (University of Hradec Kralove, Hradec Králové, CZ) and prof. Grzegorz WIELGOSIŃSKI (Lodz University of Technology, Łódź, PL) granted awards (sponsored by the Society of Ecological Chemistry and Engineering) for the best presentations. The awards for oral presentations were given to: Patrycja ŁECHTAŃSKA, M.Sc., Eng. (Lodz University of Technology, Łódź, PL) for the lecture: P. ŁECHTAŃSKA and G. WIELGOSIŃSKI: *Use of ammonium sulfate as an inhibitor of dioxins synthesis in iron ore sintering process*. Anna SZYMONIK, M.Sc. (Czestochowa University of Technology, Częstochowa, PL) for the presentation: A. SZYMONIK and J. LACH: *Pharmaceuticals in surface and drinking water* and Anna KAMIŃSKA, M.Sc. (Lodz University of Technology, Łódź, PL) for the lecture: A. KAMIŃSKA, M. JĘDRZEJCZAK and K. WOJCIECHOWSKI: *Toxicity studies of metalcomplex dyes on Daphnia pulex.*

The awards for poster presentations were given to Edyta KUDLEK, M.Sc. (Silesian University of Technology, Gliwice) for the poster: J. BOHDZIEWICZ, E. KUDLEK and M. DUDZIAK: *Changes in toxicity of water containing selected pharmaceuticals during the photocatalytic oxidation process*, to Agnieszka SZEWCZYK, M.Sc. (Institute of Ceramics and Building Material, Opole, PL) for the poster: A. SZEWCZYK, A. KŁOS, M. RAJFUR and K. EJSMONT: *Effects of eutrophication with changes of chemical composition on surface waters* and to Stanisław WACŁAWEK, M.Sc., Eng. (Technical University of Liberec, Liberec, CZ) for the poster: S. WACŁAWEK, P. HRABÁK, M. STUCHLIK, J. MACHACKOVA, L. LACINOVÁ and M. ČERNÍK: *History of Hajek site and remediation of hexachlorocyclohexanes* (*HCH*) *and chlorobenzenes* (*CB*) *contamination*.

On Saturday morning an excursion was organised to the gold mine in Złoty Stok.

Closing the conference, prof., prof. Maria and Witold Wacławek made short recapitulation. In general, ECOpole '13 was focused on monitoring of the quality of natural environment, its effects on human life, environmental education as well as application of renewable sources of energy.

They expressed gratitude to all participants for coming and taking active part in the Conference and thanked Sponsor (Ministry of Science and Higher Education, Warszawa, PL) as well as all Chairpersons of Sessions.

The organizers informed that the electronic version of the presented contributions (lecture or poster) could be published on the Conference website. They announced, that full texts of the presented papers will be published (after obtaining reviewers' positive opinions) in the successive issues of the journals *Ecological Chemistry and Engineering A* and *S* and they will be distributed to all participants. The Extended Abstracts of the presentations will be published in two subsequent issues of semi-annual *Proceedings of the ECOpole*.

At the end they invited all Colleagues to attend the ECOpole '14 Conference, which will be held in Hotel Ziemowit in Jarnoltowek, PL in the next October.

Maria Wacławek

SPRAWOZDANIE
Z ŚRODKOWOEUROPEJSKIEJ KONFERENCJI
ECOpole ’13

W dniach 23–26 października 2013 r. odbywała się w Jarnołtówku XXII Środkowoeuropejska Konferencja ECOpole’13, zorganizowana przez Towarzystwo Chemii i Inżynierii Ekologicznej (TChIE). Uczestniczyły w niej 133 osoby reprezentujące Anglię, Czechy, Niemcy, Norwegię, Polskę i Rosję, które przedstawiły 23 referaty oraz 124 postery.

Każdy z uczestników otrzymał w teczce konferencyjnej zeszyty kwartalnika *Ecological Chemistry and Engineering S* oraz *Proceedings of ECOpole,* a także CD-ROM z krótkimi informacjami o zaproszonych wykładowcach, abstraktami wystąpień oraz programem konferencji. Abstrakty wystąpień były i są dostępne na stronie webowej konferencji

ecopole.uni.opole.pl

Podobnie jak w latach poprzednich, konferencja ECOpole ’13 była poświęcona różnym aspektom ochrony środowiska przyrodniczego. Jej obrady były zgrupowane w czterech Sekcjach:

- SI Substancje chemiczne w środowisku przyrodniczym oraz ich monitoring
- SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie
- SIII Forum Młodych (FM) i Edukacja proekologiczna
- SIV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi.

W środę (23.10.2013) o godz. 19.00 konferencję otworzyli prof. Maria Wacławek (Uniwersytet Opolski) – przewodnicząca Komitetu Organizacyjnego i prof. Witold Wacławek (Towarzystwo Chemii i Inżynierii Ekologicznej, Opole) – przewodniczący Rady Naukowej Konferencji i prezes TChIE, a następnie odbył się recital gitarowy Tadeusza Pabisiaka pt.: *Od Bacha to Beatlesów*. W programie znalazły się utwory m.in. J.S. Bacha, I. Albeniza, F. Chopina, P. de Lucii, V. Gomeza, E. Lecuona, N. Paganiniego, a także J. Lennona i P. McCartneya. Publiczność dziękowała artyście za występ hucznymi oklaskami i skutecznie domagała się bisów.

W czwartek pierwszą sesję plenarną rozpoczął prof. Eiliv STEINNES (Norwegian University of Science and Technology, Trondheim, Norwegia) referatem: *Metal contamination of the terrestrial environment from long-range atmospheric transport: evidence from 35 years of research in Norway*. Następnie został wygłoszony wykład autorów Jacek NAMIEŚNIK, Łukasz MARCINKOWSKI i Adam KLOSKOWSKI (Politechnika

Gdańska, Gdańsk): *Green aspects of sample preparation techniques for isolation of organic analytes from environmental samples*. Zaproszeni wykładowcy wygłosili w czasie konferencji jeszcze trzy referaty plenarne, a mianowicie: prof. Marina V. FRONTASYEVA (Joint Institute for Nuclear Research, Dubna, Federacja Rosyjska): *Contribution of the Joint Institute for Nuclear Research to the programme of the United Nations on the study of atmospheric deposition of heavy metals in Europe based on moss analysis*, prof. Miroslav ČERNÍK (Politechnika w Libercu, Liberec, Czechy): *Technologies for groundwater remediation based on application of zero-valent iron nanoparticles* oraz prof. Władysław KAMIŃSKI i Elwira TOMCZAK (Politechnika Łódzka, Łódź): *Low-cost sorbents applications for water treatment.*

Ponadto bardzo interesujący referat przedstawił dr Z.A. SZYDŁO (Highgate School, London, Anglia): *The chemical theatre – education, enlightenment, entertainment* Spotkał się on z dużym zainteresowaniem uczestników. Na uwagę zasługują także referaty S. FRÄNZLE i A. BAUER (Internatinal School Zittau (IHI), Niemcy): *Biomonitoring and ore prospection by means of chitin and living arthropods*, S.V. GORELOVEJ, M.V. FRONTASYEVEJ, A.V GORBUNOVA, S.M. LYAPUNOVA i O.I. OKINEJ (L.N. Tolstoy TSPU, Tula, Federacja Rosyjska): *Exotic woody shrubs which can be used for bioaccumulation of technogenic pollution in urban ecosystems of non--chernozem zone of Russia*, E. TOMCZAK i A. DOMINIAK (Politechnika Łódzka, Łódź): *Historical changes in the water supply system and maintenance of drinking water quality standards in the city of Lodz*, T. OLSZOWSKIEGO (Politechnika Opolska, Opole): *Study of scavenging* pm_{10} *by large-scale precipitation (frontal rainfall*) oraz T. CIESIELCZUKA i C. ROSIK-DULEWSKIEJ (Uniwersytet Opolski, Opole): *Possibility of compost use as a sorbent of petroleum products in simulated conditions.*

W czwartek po południu odbyła się druga z kolei Sesja Posterowa. Zaprezentowano 34 plakaty. Wiele dyskusji rozpoczętych przy plakatach kontynuowano do późnych godzin wieczornych.

O 19.30 uczestnicy konferencji zostali zaproszeni na uroczystą kolację.

W piątek po południu tradycyjnie odbywało się Forum Młodych (FM). Młodzi ekolodzy, w czasie swoich wystąpień (było ich 7) poruszali i dyskutowali nad lokalnymi problemami ekologicznymi w swoich krajach. W czasie Sesji Posterowej Forum Młodych, zaprezentowano 35 posterów.

Jury w składzie prof. Maria WACŁAWEK (Uniwersytet Opolski, Opole) – przewodnicząca, prof. Marina V. FRONTASYEVA (Frank Laboratory of Neutron Physics Joint Institute for Nuclear Research, Dubna, Federacja Rosyjska), prof. Stefan FRÄNZLE (IHI, Zittau, Niemcy), prof. Bohumil VYBIRAL (University of Hradec Kralove, Hradec Králové, Czechy) oraz prof. Grzegorz WIELGOSIŃSKI (Politechnika Łódzka, Łódź) przyznało nagrody młodym pracownikom naukowym.

I nagrodę przyznano mgr inż. Patrycji ŁECHTAŃSKIEJ (Politechnika Łódzka, Łódź) za referat: P. ŁECHTAŃSKA i G. WIELGOSIŃSKI: *Use of ammonium sulfate as an inhibitor of dioxins synthesis in iron ore sintering process*.

II nagrodę uzyskała mgr Anna SZYMONIK (Politechnika Częstochowska, Częstochowa) za prezentację ustną: A. SZYMONIK i J. LACH: *Pharmaceuticals in surface and drinking water.*

III nagrodę przyznano mgr Annie KAMIŃSKIEJ (Politechnika Łódzka, Łódź) za referat: A. KAMIŃSKA, M. JĘDRZEJCZAK i K. WOJCIECHOWSKI: *Toxicity studies of metalcomplex dyes on Daphnia pulex.*

Ponadto przyznano trzy nagrody za plakaty.

I nagrodę otrzymała mgr Edyta KUDLEK (Politechnika Śląska, Gliwice) za plakat J. BOHDZIEWICZ, E. KUDLEK i M. DUDZIAK: *Changes in toxicity of water containing selected pharmaceuticals during the photocatalytic oxidation proces*

II nagrodę – mgr Agnieszka SZEWCZYK (Ośrodek Inżynierii Procesowej, Materiałów Budowlanych, Opole) za plakat A. SZEWCZYK, A. KŁOS, M. RAJFUR i K. EJSMONT: *Effects of eutrophication with changes of chemical composition on surface waters*

III nagrodę uzyskał mgr inż. Stanisław WACŁAWEK (Politechnika w Libercu, Liberec, Czechy) za plakat S. WACŁAWEK, P. HRABÁK, M. STUCHLIK, J. MACHACKOVA, L. LACINOVÁ i M. ČERNÍK: *History of Hajek site and remediation of hexachlorocyclohexanes (HCH) and chlorobenzenes (CB) contamination.*

W przerwach między obradami licznie odwiedzano ekspozycję książek opublikowanych przez Wydawnictwa Naukowo-Techniczne (WNT) oraz książek i czasopism wydanych przez Towarzystwo Chemii i Inżynierii Ekologicznej w Opolu.

W sobotę została zorganizowana wycieczka do kopalni złota w Złotym Stoku.

Na zakończenie konferencji prof. prof. Maria i Witold Wacławek podziękowali wszystkim uczestnikom za udział, a szczególnie gorąco osobom mającym wystąpienia oraz przewodniczącym obradom. Słowa gorących podziękowań zostały także skierowane do członków Komitetu Organizacyjnego konferencji za duży, wielomiesięczny wkład ich pracy.

Wszyscy uczestnicy konferencji zostali zaproszeni do publikacji swoich prac. Organizatorzy zapewnili, że pełne artykuły z wystąpień konferencyjnych będą sukcesywnie publikowane w *Ecological Chemistry and Engineering A* oraz *S*. Poinformowali też, że rozszerzone streszczenia ukażą się w półroczniku *Proceedings of ECOpole*.

Organizatorzy konferencji zaprosili wszystkich do udziału w dwudziestej trzeciej konferencji ECOpole. Zapowiedzieli oni, że aktywni uczestnicy Forum Młodych konferencji ECOpole '14 mogą znowu liczyć na znaczne obniżenie opłaty konferencyjnej.

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

INVITATION FOR
ECOpole ’14 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 23rd annual Central European Conference ECOpole ’14, which will be held in 15–18.10.2014 (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 (6–8 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 2014** and for the Extended Abstracts: **1st October 2014**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2014**) 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.

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 Conference website).

After the ECOpole ’14 Conference it will be possible to publish electronic version of presented contributions (oral presentations as well as posters) on this site.

Further information is available from:
Prof. dr hab. inż. Maria Wacławek
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of ECOpole '14 Conference
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Conference series

1. 1992 Monitoring '92 Opole
2. 1993 Monitoring '93 Turawa
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18. 2009 CEC ECOpole '09 Piechowice
19. 2010 CEC ECOpole '10 Piechowice
20. 2011 CEC ECOpole '11 Zakopane
21. 2012 CEC ECOpole '12 Zakopane
22. 2013 CEC ECOpole '13 Jarnołtówek

ZAPRASZAMY DO UDZIAŁU W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI ECOpole ’14 W DNIACH 15–18 X 2014 r.

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

Będzie to **dwudziesta trzecia z rzędu** konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotyczącym różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w Hotelu Ziemowit w Jarnołtówku.

Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole ’14 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 6–8 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 2014 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 31 lipca 2014 r. na tej stronie. 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

tchie.uni.opole.pl

Po konferencji zostaną wydane 6–8-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te winny być przesłane do **1 października 2014 r.** Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej.

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:

ecopole.uni.opole.pl

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

Prof. dr hab. inż. Maria Wacławek
Przewodnicząca Komitetu Organizacyjnego
Konferencji ECOpole '14

Wszelkie uwagi i zapytania można kierować na adres:
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[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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