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INFLUENCE OF SALINE STRESS ON THE ABUNDANCE OF LIME APHID (*Eucallipterus tiliae* L.) ON THE LEAVES OF STREET TREES - CRIMEAN LINDEN

WPŁYW STRESU SOLNEGO NA LICZEBNOŚĆ MSZYC (*Eucallipterus tiliae* L.) NA LIŚCIACH DRZEW ULICZNYCH *TILIA* 'EUCHLORA'

Abstract: This publication presents the influence of soil salinity on the abundance of aphids on the leaves of street trees in cities. The objects of research were trees of Crimean Linden (*Tilia* '*Euchlora*') planted at Zwirki and Wigury Street in Warsaw. The research included the evaluation of the trees' condition, the counting of the number of Lime Aphid (*Eucallipterus tiliae* L.), as well as the determination of chlorine and nitrogen content in the leaves. The research revealed a statistically significant influence of chlorine content in the leaves on the deterioration of their condition. The increased content of chlorine in the leaves was accompanied by a decrease in the number of aphids. This relationship was statistically significant. No nitrogen deficiency in the leaves was detected. No statistically relevant relationship between the nitrogen content and the condition of the trees was observed. There was a weak negative correlation which, however, was statistically insignificant. Using the regression function it was determined that the increase in chlorine content in leaves by 1% (from 1.0 to 2%) resulted in a decrease in the abundance of aphids by 49%. What is more, a statistically significant ($p = 0.032$) influence of nitrogen content on the abundance of aphids was proved. The increase of this element by 1% (from 2.5 to 3.5%) was accompanied by the increase in the number of aphids by 90%.

Keywords: *Tilia* 'Euchlora', *Eucallipterus tiliae* L., aphids, nitrogen, chlorine, salt stress

Street trees planted in cities are subjected to unfavorable conditions for growth and development. The use of sodium chloride to de-ice the roads in wintertime, as well as water deficiency and air pollution result in a worsening condition of street trees and their withering away on a big scale. An important factor is also the occurrence of pests with sucking mouthparts - mainly aphids and tetranychus [1-3]. In Liverpool 39% of trees planted in the last few years died no later than within five years of being planted [4]. The research carried out in Warsaw by Dmuchowski et al [5] proved that within the last 34 years more than a half of street trees have withered away. The biggest loss was observed for species such as: *Sorbus aucuparia* (94%), *Acer pseudoplatanus* (83%), *Tilia cordata* (65%) and *Tilia* 'Euchlora' (62%). The smallest loss was observed for *Tilia platyphyllos* (44%).

The result of both biotic and abiotic stresses, to which the street trees are subjected, changes in their morphology as well as in physiological and biochemical processes. Not only does it contribute to the deterioration of decorative qualities of the trees, but also, which is more important, it obstructs their biological functions [6, 7].

The aim of this research was the determination of the influence of saline stress on the abundance of Lime Aphid (*Eucallipterus tiliae* L.) on the leaves of street trees - Tilia 'Euchlora'.

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Material and methods

The objects of research were Crimean Linden (48 specimens) planted at Zwirki and Wigury Street in Warsaw. The leaves condition was evaluated in mid-September using the seven-grade scale method of direct observation [8]. The samples of leaves were collected in mid-July from the outer perimeter of the tree crown, at the height of 2÷4 meters. The chlorine amount was determined using the method of potentiometric titration with ion-selective electrode and ion-meter of Orion Type 701a [9]. The nitrogen concentration was determined using the Kjeldahl method with analyzer 1035 Foss Tecator.

The number of Lime Aphid (*Eucallipterus tiliae* L.) on the leaves was counted three times, on dates 28.05, 11.06 and 28.06 of 2010. In the final calculations, only the measurements of the abundance of aphids on the leaves made in May were taken into account. In observations made in June the number of aphids was very small. The average number of aphids on a leaf was estimated on the basis of observation of 40 randomly chosen leaves (10 per each side), separately for each of the trees.

In order to compare the average number of aphids with the concentrations of nitrogen and chlorine in the leaves under different health conditions, univariate analysis of variance was applied. Multiple comparisons were made using the Tukey procedure. On the basis of the analysis mentioned above the three groups of means were separated. For the analysis the significance level was assumed at 0.05 [10].

Results and discussion

The concentration of chlorine in the leaves of Crimean Linden ranged between 0.89% and 1.95% (Fig. 1). On the basis of literature review one can conclude that for all the studied trees the chlorine toxicity threshold was exceeded (> 0.6%) [11, 12]. The presence of chlorine in the leaves results in the initially invisible changes inside the plant cells, and with the increasing amounts of this ion, in morphological changes such as chlorosis visible on the leaf lamina. Research conducted in Warsaw confirmed that even minor salinity of the soil can cause necrosis on the edges of leaves, and result in rapid withering and death of trees [13, 14]. The research confirmed a statistically relevant influence of chlorine concentration in the leaves on the deterioration of their condition. The trees with the lowest leaf-damage index contained on average 0.89% of chlorine while “sick” trees (index 4-5) contained on average 1.93% of this element. Similar results were reached by Suplat [14] and Dmuchowski and Badurek [13].

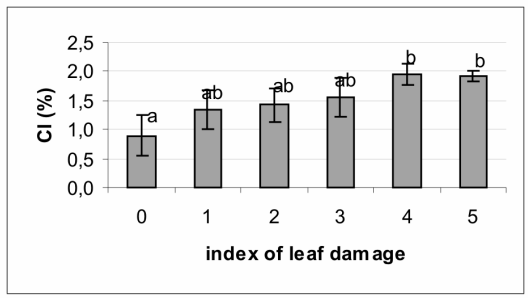

Fig. 1. The comparison of the average concentration of chlorine in leaves in different health condition

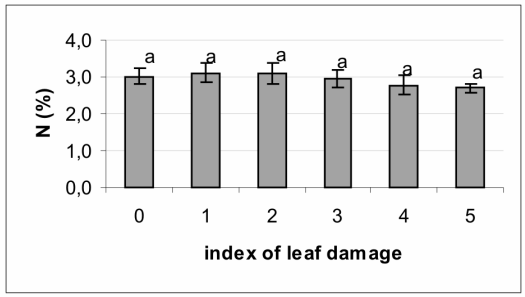

Fig. 2. The comparison of the average concentration of nitrogen in leaves in different health condition

Leaves of Crimean Linden contained from 2.70 to 3.02% of nitrogen (Fig. 2). Consequently, no deficiency levels (1.7÷2.1%) [15, 16] of this element in the examined leaves were observed. No statistically relevant relationship between the condition of the trees and the concentration of nitrogen in the leaves was detected. However, it was observed that the relatively "healthy" leaves contained higher amounts of that element (on average 3.02%) than the leaves qualified as "sick" (on average 2.73%). Markiewicz and Kleiber [17] did not record any relevant influence of salinity on the nitrogen content in the outer leaves of lettuce. Nevertheless according to Kachel-Jakubowska [18], the concentration of nitrogen is correlated with the chlorophyll content. Bach et al [6] indicated that in "sick" trees the photosynthesis does not take its normal course. The deterioration of the photosynthesis intensity results mainly from the leaf damage (withering, discoloration) obstructing the transportation and supply of carbohydrates, nitrogen compounds and plant hormones [19].

The aphids were counted three times, on dates 28.05, 11.06 and 28.06 of 2010. However, only during the observation made in May the Lime Aphid appeared in relatively large numbers. On average, the number of 5-14 aphids was observed on one leaf of Crimean Linden. In other observations the number of aphids was very small (on average 0-1 on one leaf). No statistically significant relationship between the abundance of aphids and the condition of trees was detected. Many authors claims that aphids on the linden trees develop better during cool and humid summers [20, 21]. In May 2010 the weather was quite humid and cold and consequently it is possible that the weather conditions resulted in the relatively large number of aphids in May.

Table 1

The comparison of the average number of aphids on the leaves in different health condition

Index of leaf damage	28.05.2010	11.06.2010	28.06.2010
0	13.83 a	1.35 a	0.51 a
1	11.25 a	1.55 a	1.08 a
2	11.81 a	1.52 a	0.78 a
3	9.13 a	1.31 a	0.61 a
4	8.85 a	1.96 a	0.29 a
5	4.71 a	0.19 a	0.54 a

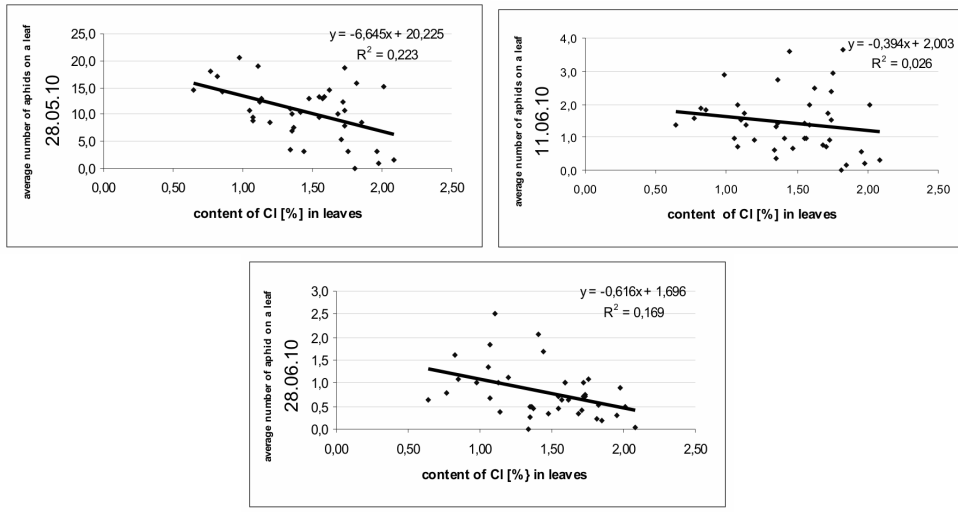

Fig. 3. The relation between chlorine content and the average number of aphids on the leaf

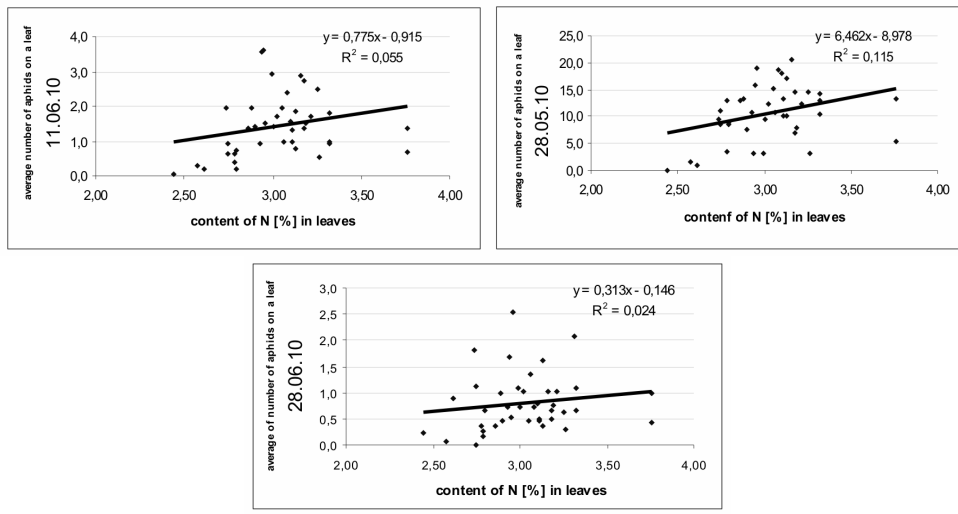

Fig. 4. The relation between chlorine content and the average number of aphids on the leaf

In this research a negative correlation was detected between the chlorine content and the number of aphids on the leaf. Using the regression function (Fig. 3) it was determined that the increase in chlorine content in the leaves by 1% (from 1.0 to 2%) resulted in a decrease in the abundance of aphids by 49%. Furthermore, a statistically relevant ($p = 0.032$) influence of nitrogen content on the abundance of aphids was proved (Fig. 4). The increase of this element by 1% (from 2.5 to 3.5%) was accompanied by the increase in the number of aphids by 90%.

A change in the osmotic pressure of soil solution, which results in physiological drought, is a consequence of the salinity of the soil [22]. At the same time, water deficiency in plants results in an increase in the level of contamination by pests [23]. This is connected with the increased level of nitrogen compounds which is why those plants are preferred by phytophage pests [24]. In the leaves of linden trees planted in the vicinity of roads the relationship between sugars and phenols is also changed [21]. Hale et al [25] conducted research on the influence of drought stress of grasses on the abundance of bird cherry oat aphid (*Rhopalosiphum padi*). They concluded that the abundance of aphids is correlated with the concentration of nitrogen compounds in the phloem solution. Moreover, the aphids can modify the accumulation level of nitrogen compounds in the leaves on which they prey. Some arthropods change the chemical composition of the leaves of their host plants by saliva injection. Aphids, eriophyid mites and other phytophage pests with piercing mouthparts can cause influx of nitrogen compounds and consequently increase the level of nitrogen in those plants [24].

Honeydew produced by aphids can cause limitation of the photosynthesis and transpiration in the leaves of trees. The high abundance of aphids persisting for long periods of time on plants can deteriorate the condition (vigor) of the trees severely attacked by such pests [6]. For this reason it seems necessary to continue the research on the influence of biotic stress and salinity on the abundance of pests in the leaves of street trees.

Conclusions

1. No nitrogen deficiency levels were observed. The content of this element did not influence the condition of the trees.
2. A statistically significant influence of nitrogen concentration in the leaves on the abundance of aphids was detected. Using the regression function it was proved that the increase in the nitrogen content by 1% (from 2.5 to 3.5%) results in a decrease of the abundance of aphids by 90%.
3. The chlorine toxicity threshold in the leaves of Crimean Linden was exceeded (> 0.6%). Relatively "healthy" trees (leaf-damage index 0-3) contained less chlorine than the "sick" trees (index 4-5).
4. The increased content of chlorine in the leaves was accompanied by a decrease in the number of aphids. Using the regression function it was indicated that the increase in chlorine content in the leaves by 1% (from 1.0 to 2%) resulted in a decrease in the abundance of aphids by 49%.

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WPŁYW STRESU SOLNEGO NA LICZEBNOŚĆ MSZYC (*Eucallipterus Tiliae* L.) NA LIŚCIACH DRZEW ULICZNYCH *TILIA* 'EUCHLORA'

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Abstrakt: Przedstawiono wpływ zasolenia gleby na liczebność mszyc na liściach drzew miejskich. Przedmiotem badań były drzewa z gatunku lipa krymska (*Tilia* 'Euchlora'), rosnące w pasie międzyjezdniowym al. Żwirki i Wigury w Warszawie. Badania polegały na ocenie stanu zdrowotnego drzew, zliczaniu mszyc zdobniczki lipowej (*Eucallipterus Tiliae* L.) oraz na określeniu zawartości chloru i azotu w liściach. Stwierdzono statystycznie istotny wpływ zawartości chloru w liściach na pogorszenie ich stanu zdrowotnego. Zwiększonej zawartości chloru w liściach towarzyszyło zmniejszenie liczebności mszyc. W przypadku zawartości azotu

w liściach nie stwierdzono występowania poziomów niedoborowych. Nie wykazano statystycznie istotnej zależności między zawartością azotu a stanem zdrowotnym drzew. Między zawartością chloru i azotu występowała słaba zależność ujemna, która jednak była nieistotna statystycznie. Na podstawie funkcji regresji stwierdzono, iż wzrost zawartości chloru w liściach o 1% (z 1,0 do 2,0%) powodował spadek liczebności mszyc o 49%. Wykazano także statystycznie istotny (p = 0,032) wpływ zawartości azotu na liczebność mszyc. Wraz ze wzrostem zawartości tego pierwiastka w liściach o 1% (z 2,5 do 3,5%) zwiększała się liczba mszyc o 90%.

Słowa kluczowe: *Tilia* 'Euchlora', *Eucallipterus Tiliae* L., mszyce, azot, chlor

Marie BJELKOVA[1], Martina VETROVCOVA[2], Miroslav GRIGA[2] and Petr SKARPA[3]

EFFECT OF SEWAGE SLUDGE IN SOIL ON Cd, Pb AND Zn ACCUMULATION IN *Linum usitatissimum* L.

WPŁYW APLIKACJI OSADÓW ŚCIEKOWYCH DO GLEBY NA AKUMULACJĘ Cd, Pb I Zn W LNIE ZWYCZAJNYM (*Linum usitatissimum* L.)

Abstract: Sewage sludge is the product of the process of wastewater treatment. Sludge may be considered hazardous waste requiring costly disposal procedures, or may be perceived as a source of nutrients for use on agricultural land. Experiments were carried out in simulated natural conditions in pots set in the land to a depth of 50 cm with variations of graded mixture of natural sediments and soils. Sewage sludge sedimentation was added into the weighed quantity of soil in the proportions: sludge - soil = 1:2 (var. K1), 1:3 (var. K2), 1:4 (var. K3), 1:5 (var. K4), 1:6 (var. K5). Control variant (K0) without the presence of sewage sludge has also been sown with all varieties. Studied crop were the varieties of flax and linseed. Flax and linseed varieties variously accumulated particular metallic elements, the highest concentrations were recorded for Zn, followed by the Pb and Cd. The lowest concentrations of Cd and Pb were analyzed in the seed (0.121 $mg \cdot kg^{-1}$) and the highest concentrations of Cd and Pb were detected in the stem (Cd = 0.396 $mg \cdot kg^{-1}$) and capsules (Pb = 1.881 $mg \cdot kg^{-1}$). The highest concentration of Zn was found in the capsule (115.015 $mg \cdot kg^{-1}$) and lowest in the root (33.782 $mg \cdot kg^{-1}$). Trend of accumulation of Cd was: stem>capsule>root>seed, Pb: capsule>stem>root>seed, Zn: capsule >seed>root>stem. The results of studied experiments show that the particular varieties of fiber and linseed have different variability in the ability to draw heavy metals from the soil and consequently different phytoremediation potential.

Keywords: *Linum usitatissimum* L., flax, linseed, cadmium, lead, zinc

Sewage sludge is the product of the process of wastewater treatment. Sludge may be considered hazardous waste requiring costly disposal procedures, or may be perceived as a source of nutrients for use on agricultural land. For application of sewage sludge on agricultural land at the Czech Republic the concentration limits of chosen risk elements have to be respected and the only these sewage sludges which are in the agreement with the respective regulation are allowed to be used. Limit (maximum) concentrations in sludge are for Cd = 5 $mg \cdot kg^{-1}$, Cu = 500 $mg \cdot kg^{-1}$, Pb = 200 $mg \cdot kg^{-1}$, Zn = 2500 $mg \cdot kg^{-1}$, As = 30 $mg \cdot kg^{-1}$, Cr = 200 $mg \cdot kg^{-1}$ and Ni 100 $mg \cdot kg^{-1}$ d.m. Bioavailability of heavy metals is not directly correlated with their total concentrations in soil or sludge. Availability of heavy metals from sewage sludge to the plants is mainly determined by soil properties. Mobility of metals in the soil after application of sewage sludge depends mainly on chemical and physical properties of sludge-soil. Metals originated from sewage sludge are mainly accumulated in the surface layers of soil and Zn is the most accessible for the organisms. Sewage sludges contain high levels of organic and inorganic nutrients, but the availability of toxic metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in cultivated crops [1, 2] is considered to be the main problem. Knowledge of the crops characteristics on contaminated sites and their potential ability to transfer metal contaminants in the harvested plant parts can be a very important finding for future phytoremediation applications.

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Studies in the plants [3] for the ability to accumulate Cd, Pb and Zn in soil enriched sewage sludge showed differences between crops and their varieties.

Materials and methods

The experiment was conducted at the agricultural research institute Agritec, Ltd. of Sumperk, located in the middle Europe in the Northern Moravia part of the Czech Republic at 49°58'21.213"N latitude, 16°58'0.341"E, longitude and 329 m above the sea level. The experiment was conducted during the growing season April-August 2005, 2006 and 2007. This growing periods of the years were characterized by average monthly temperatures between 8.3ºC and 20.5ºC. Average monthly maximal temperatures fluctuated between 20.4 and 35.2 and the average monthly minimal temperatures between –6.0ºC and 8.0ºC. The total rainfall was 297.5 mm in 2005, 365.7 mm in 2006 and 247.5 mm in 2007, respectively compared with long-term average rainfall 339.5 mm in the monitored growing periods. Experiments were carried out in simulated natural conditions in pots set in the land to a depth of 50 cm with variations of graded mixture of natural sediments and soils. Sewage sludge sedimentation was added into the weighted quantity of soil in the proportions: sludge-soil = 1:2 (var. K1), 1:3 (var. K2), 1:4 (var. K3), 1:5 (var. K4) and 1:6 (var. K5). Control variant (K0) without the presence of sewage sludge has also been sown with all varieties. Jitka, Laura, Viola, Mercury, Venica, Hermes, Jordan, Escalina, Viking, Tabor, Bonet, Agatha, Super, Marylin, Ilona, Elektra, Atalante, Flanders, Lola, Biltstar were the studied flax and linseed varieties. Harvested plants were dried, separated into the stem, capsules, root and seed and analyzed.

Table 1

Chemical characterization of natural soil used in the experiments

	pH/$CaCl_2$	**K**	**P**	**Mg**	**Ca**	**N-NH_4**	**N-NO_3**	**Cd**	**Pb**	**Zn**
[mg·kg^{-1} d.m.]	6.75	171	73	201	2047	3.89	6.5	0.25	32.8	56.4

Table 2

Chemical characterization of used sewage sludge

	[mg·kg^{-1} d.m.]								**[%]**	**[mg·kg^{-1} d.m.]**		**[g·kg^{-1} d.m.]**			
pH	**Pb**	**Cd**	**Cu**	**Zn**	**Cr**	**Ni**	**As**	**Hg**	**N total**	**N-NH_4**	**N-NO_3**	**P total**	**Ca**	**Mg**	**K**
8.05	57.6	1.7	198	1250	155	28.1	4.3	1.9	4.8	9410	49.9	28	33.3	6.27	5.05

The digestion of plant materials was performed in a microwave oven operating system (Milestone, ETHOS D) with an energy output 0÷400 W (0÷100% potency, respectively). Approximately 0.5 g of dry plant materials were placed into the teflon microwave digestion vessels, then 5 cm^3 of 65% HNO_3 and 1 cm^3 of 30% H_2O_2 were added to each sample. Plant samples were digested using the optimatized microwave programs. After cooling to room temperature the digested samples were diluted to a final volume of 25 cm^3 with deionized water. Blank samples were prepared simultaneously. These solutions were stored in a refrigerator at 4°C until the analysis was carried out. The total contents of elements (Cd, Pb) in the digests were determined by graphite furnace atomic absorption spectroscopy (SOLLAR M, Unicam Ltd., Cambridge, U.K.) equipped with Zeeman and deuterium background correctors, a graphite furnace GF95 and an auto-sampler. For the determination of Zn there was used flame atomic absorption spectroscopy. For this work, the deuterium lamp was used as background corrector for determination of Zn and Cd, the Zeeman

corrector was employed for determination of Pb. The wavelengths used for quantification were: Cd = 228.8 nm; Pb = 217.0 nm; Zn = 213.9 nm. Certified reference materials IRM 9035 kohlrabi-haulm UKZUZ Brno were applied for quality assurance of analytical data**.** The results data were statistically analyzed by using the statistical package program Statistica, using analysis of variance and multiple comparisons and correlation.

Results and conclusions

The highest concentration was found in zinc (15.51÷375.2 mg·kg^{-1} d.m.), followed by lead (Pb) with (0.01÷5.85 mg·kg^{-1} d.m.) and the lowest concentration was detected in cadmium (0.007÷5.22 mg·kg^{-1} d.m.). Individual studied metals were variously accumulated into organs of flax and linseed. The application of sewage sludge influenced the level of Cd content in all flax organs. Lead and zinc content in flax and linseed plants fluctuated in the respective variants and did not show significant increasing tendency in all organs by the increasing content of sewage sludge into the soil similarly as Balik et al [4] investigated by Zn accumulation in oat. By mutual evaluation of concentration of heavy metals in different organs the highest accumulation of cadmium was found in stem, lead (Pb) and zinc in capsules. On the contrary, the lowest concentration of cadmium and lead (Pb) was detected in seed and the lowest concentration of zinc was found in root. Cadmium was more accumulated by linseed varieties, whereas lead (Pb) and zinc were more accumulated by flax varieties. Variant with the highest sewage sludge content 1K significantly ($p \geq 0.05$) concentrated cadmium into all organs in contrary to control variant of Table 8. The found Cd concentration indicates trend of accumulation in the direction of stem>capsule>root>seed, similarly to work Jiao et al [5], who found decreasing direction of accumulation at harvest time: stem>seed. The trend of lead (Pb) transport was following: capsules>stem>root > seed. The concentration of lead (Pb) in root was equal in all variants enriched by sludge. However, it was significantly ($p \geq 0.05$) lower in comparison with the control. On the other hand, the concentration of lead (Pb) in a seed had completely opposite tendency and varied in stem and capsules. The trend of zinc concentration was: capsule>seed>root>stem and the highest was in the capsule, but between the individual variant was balanced and insignificantly higher in the control variant. The zinc content in a stem was different in individual variants with significantly highest content of the control. Zinc accumulated in root shows significant ($p \geq 0.05$) influence on variants with higher content of sludge (Tab. 3). While studying concentration of zinc in a seed there was found significantly ($p \geq 0.05$) increasing content of element with increasing amount of sludge in soil. Table 3 represents total accumulation of heavy metals, so-called absorption factor, that is absorption of risk element by crop per area unit [g·ha^{-1}]. By biomass of aboveground mass, on contrary of total crop mass, was absorbed off 89% Cd, 85% Pb and 91% Zn. Stem had the highest absorption factor of all three elements (mean 2.176 g Cd·ha^{-1}, 4.053 g Pb·ha^{-1} and 170.369 g Zn·ha^{-1}). Cd absorption was higher in linseed varieties (except of root), in contrary to Pb and Zn absorption was higher from flax (except of capsules and seeds). These trends of absorption by individual organs of flax and linseed plants were found out from resultant analyses of gained data: Cd = stem>root>capsule>seed, Pb = stem>capsule>root>seed, Zn = stem>capsule>seed>root. Absorption of Cd by all parts of plant was significant ($p \geq 0.05$) for variants with higher content of sludge in soil.

Table 3

Heavy metal (Cd, Pb, Zn) uptake/accumulation (mg Cd, Pb, Zn kg^{-1} d.m.; g Cd, Pb, Zn ha^{-1}) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested cultivars (data for 20 flax and linseed cvs.). Analysis of variance; mature plants; field-simulated experiment 2005-2007

	Root	**Stem**	**Capsule**	**Seed**	**Root**	**Stem**	**Capsule**	**Seed**
	[mg Cd·kg^{-1}]				**[g Cd·ha^{-1}]**			
1K = 1:2	0.376^{b}	0.566^{c}	0.535^{c}	0.164^{e}	0.420^{b}	3.972^{b}	0.428^{c}	0.147^{c}
2K = 1:3	0.323^{a}	0.444^{bc}	0.514^{bc}	0.154^{de}	0.312^{a}	2.489^{a}	0.414^{c}	0.166^{c}
3K = 1:4	0.313^{a}	0.375^{ab}	0.409^{b}	0.128^{cd}	0.297^{a}	1.960^{a}	0.321^{b}	0.130^{bc}
4K = 1:5	0.309^{a}	0.335^{ab}	0.285^{a}	0.111^{bc}	0.288^{a}	1.560^{a}	0.216^{a}	0.123^{bc}
5K = 1:6	0.302^{a}	0.296^{a}	0.265^{a}	0.092^{ab}	0.312^{a}	1.447^{a}	0.220^{a}	0.088^{ab}
Control	0.298^{a}	0.362^{ab}	0.263^{a}	0.074^{a}	0.279^{a}	1.627^{a}	0.224^{a}	0.056^{a}
	Root	**Stem**	**Capsule**	**Seed**	**Root**	**Stem**	**Capsule**	**Seed**
	[mg Pb·kg^{-1}]				**[g Pb·ha^{-1}]**			
1K = 1:2	1.135^{a}	0.929^{ab}	1.699^{a}	0.573^{b}	1.247^{bc}	6.065^{b}	1.469^{a}	0.606^{b}
2K = 1:3	1.045^{a}	0.886^{ab}	1.716^{ab}	0.657^{b}	0.984^{ab}	4.082^{a}	1.345^{a}	0.785^{b}
3K = 1:4	1.037^{a}	0.887^{ab}	1.713^{ab}	0.612^{b}	0.911^{a}	3.864^{a}	1.399^{a}	0.685^{b}
4K = 1:5	1.067^{a}	0.832^{ab}	1.982^{b}	0.593^{b}	0.954^{ab}	3.312^{a}	1.526^{a}	0.695^{b}
5K = 1:6	1.103^{a}	0.748^{a}	2.271^{c}	0.547^{b}	1.009^{ab}	3.408^{a}	1.860^{b}	0.655^{b}
Control	1.574^{b}	0.901^{b}	1.907^{ab}	0.328^{a}	1.480^{c}	3.587^{a}	1.645^{ab}	0.237^{a}
	Root	**Stem**	**Capsule**	**Seed**	**Root**	**Stem**	**Capsule**	**Seed**
	[mg Zn·kg^{-1}]				**[g Zn·ha^{-1}]**			
1K = 1:2	37.893^{b}	39.085^{c}	117.638^{a}	74.811^{b}	37.753^{b}	201.409^{b}	95.831^{a}	70.388^{b}
2K = 1:3	36.266^{b}	35.804^{ab}	112.596^{a}	74.131^{b}	31.369a	169.973^{ab}	91.689^{a}	69.161^{b}
3K = 1:4	36.321^{b}	36.389^{bc}	109.012^{a}	74.229^{b}	30.925a	159.728^{a}	87.910^{a}	67.894^{b}
4K = 1:5	32.193^{a}	34.010^{ab}	116.041^{a}	70.867^{b}	28.795a	139.656^{a}	91.797^{a}	65.107^{b}
5K = 1:6	30.925^{a}	32.759^{a}	116.468^{a}	71.595^{b}	29.846a	151.355^{a}	101.151^{a}	68.433^{b}
Control	29.092^{a}	46.713^{d}	118.333^{a}	61.426^{a}	27.559a	200.091^{b}	99.684^{a}	42.769^{a}

$p \leq 0.05$ - statistical significance at a 95% level of significance. Variants with identical letters express statistically insignificant differences

Table 4

Correlation HMs between individual plant organs

	Cd				**Pb**				**Zn**			
	Root	**Stem**	**Cap.**	**Seed**	**Root**	**Stem**	**Cap.**	**Seed**	**Root**	**Stem**	**Cap.**	**Seed**
Root		0.41	–0.01	0.13		–0.07	0.06	–0.46		0.32	0.41	–0.04
Stem	**0.41**		0.15	0.12	–0.07		0.27	0.09	0.32		0.40	–0.26
Capsule	–0.01	0.15		0.23	0.06	0.27		–0.18	0.41	0.40		–0.23
Seed	0.13	0.12	0.23		**–0.46**	0.09	–0.18		–0.04	–0.26	–0.23	

Absorption of Pb was above all significant ($p \geq 0.05$) for variant 1K and absorption of Zn was after application of sewage sludge significant only for root, stem and seed also in variant 1K. When studying extract of cadmium from soil substrate and sewage sludge Piotrowska and Cyplik et al [5] came to similar conclusions. They learned increased content of Cd in root. By mutual evaluation of accumulation of monitored heavy metals there was found correlative dependence of Cd accumulation into stem and root ($r = 0.414$) and correlation in accumulation Pb between roots and stem ($r = –0.456$) and stem and capsules ($r = 0.411$) - see Table 4. The results show, that individual varieties of flax and linseed have different variability in ability to accumulate heavy metals from soil. Variety of linseed Flanders showed the highest concentration of Cd in root, capsules and seed (Tab. 5). This variety had significantly ($p \geq 0.05$) higher concentration Pb in seed. In variety of flax

Jitka was found the highest concentration of Pb in stem and capsules (Tab. 6). An interesting fact was, that the highest concentrations of Zn were always found in flax varieties (root - Viola, stem - Marylin, capsule - Hermes, seed - Jordan) (Tab. 7), but by mathematics analyses of calculation of absorption factor, the highest found absorption in root and stem was by variety of flax Jordan (root: 40.191 g·ha^{-1}, stem: 238.298 g·ha^{-1}), but linseed Biltstar (145.187 g·ha^{-1}) drew off more into capsules and variety linseed Atalante (105.443 g·ha^{-1}) - seed. The variety of flax Jordan presents the highest accumulative potential of Pb in stem (5.812 g·ha^{-1}), variety of linseed Atalante in root (1.435 g Pb·ha^{-1}), variety of linseed Biltstar in capsules (2.414 g Pb·ha^{-1}) and variety of linseed Flanders in seed (1.028 g Pb·ha^{-1}) (Tab. 6). Linseed Flanders had higher accumulative potential Cd in seed (0.234 g·ha^{-1}). Stem and capsules absorbed more Cd by linseed Biltstar (3.986 g·ha^{-1}, 0.573 g·ha^{-1}) (Tab. 5). By monitoring of studied heavy metals during years there was found out various significant ($p \geq 0.05$) influence on their concentration an accumulation into parts of flax.

Table 5

Cadmium uptake/accumulation (mg Cd kg^{-1} d.m.; g Cd ha^{-1}) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested variant. Mean; mature plants; field-simulated experiment 2005-2007

Variety	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
	[mg Cd mg·kg^{-1}]				[g Cd·ha^{-1}]			
Hermes	0.338	0.320	0.446	0.103	0.396	1.828	0.271	0.089
Jitka	0.308	0.445	0.414	0.159	0.238	2.719	0.338	0.118
Venica	0.319	0.316	0.221	0.100	0.364	1.917	0.177	0.122
Merkur	0.303	0.340	0.376	0.100	0.272	1.589	0.259	0.078
Bonet	0.293	0.408	0.390	0.103	0.236	2.127	0.218	0.086
Tábor	0.347	0.449	0.394	0.111	0.314	2.629	0.295	0.110
Viola	0.369	0.368	0.276	0.096	0.310	2.218	0.198	0.075
Viking	0.359	0.352	0.417	0.095	0.378	1.888	0.366	0.082
Agatha	0.346	0.477	0.423	0.143	0.409	3.518	0.308	0.130
Escalina	0.277	0.317	0.386	0.100	0.276	1.747	0.295	0.104
Ilona	0.312	0.377	0.366	0.108	0.323	2.004	0.214	0.092
Super	0.286	0.356	0.348	0.128	0.256	1.506	0.244	0.097
Elektra	0.320	0.326	0.307	0.087	0.380	2.166	0.181	0.056
Marylin	0.366	0.417	0.434	0.121	0.425	2.257	0.368	0.115
Jordán	0.277	0.384	0.359	0.132	0.328	2.697	0.292	0.096
Laura	0.315	0.383	0.334	0.118	0.337	1.885	0.262	0.119
Atalante	0.305	0.433	0.412	0.142	0.304	2.418	0.432	0.227
Flanders	0.253	0.351	0.465	0.181	0.232	1.176	0.433	0.234
Lola	0.349	0.430	0.450	0.119	0.230	1.301	0.351	0.188
Biltstar	0.363	0.681	0.353	0.168	0.353	3.986	0.573	0.149

Table 6

Lead uptake/accumulation (mg Pb kg^{-1} d.m.; g Pb ha^{-1}) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested variant. Mean; mature plants; field-simulated experiment 2005-2007

Variety	Root	Stem	Capsule	Seed	Root	Stem	Capsule	Seed
	[mg Pb mg·kg^{-1}]				[g Pb·ha^{-1}]			
Hermes	1.183	0.808	2.117	0.557	1.256	3.949	1.430	0.558
Jitka	1.073	1.087	2.343	0.600	0.892	5.679	2.029	0.491
Venica	1.184	0.855	1.609	0.556	1.239	4.725	1.336	0.791
Merkur	1.305	0.927	1.754	0.526	1.076	4.203	1.283	0.489
Bonet	0.983	0.792	1.927	0.488	0.769	3.410	1.312	0.503

Tábor	1.081	0.781	1.773	0.489	0.922	3.930	1.378	0.550
Viola	1.241	0.895	2.018	0.441	1.063	5.191	1.451	0.420
Viking	1.192	0.835	1.683	0.494	1.289	4.431	1.688	0.554
Agatha	1.075	0.889	1.595	0.551	1.265	4.997	1.260	0.577
Escalina	1.231	0.905	2.145	0.584	1.183	4.573	1.681	0.680
Ilona	1.137	0.868	2.252	0.552	0.971	4.053	1.425	0.537
Super	1.260	0.816	1.942	0.569	1.034	3.132	1.489	0.480
Elektra	1.135	0.717	1.804	0.610	1.209	3.949	1.120	0.444
Marylin	0.988	0.779	1.961	0.561	1.029	4.124	1.585	0.542
Jordán	1.172	0.961	1.989	0.551	1.341	5.812	1.508	0.399
Laura	1.022	0.958	1.782	0.546	1.046	4.329	1.496	0.663
Atalante	1.399	0.778	1.555	0.557	1.435	2.945	1.647	0.993
Flanders	1.171	0.873	1.802	0.706	1.042	2.330	1.798	1.028
Lola	1.279	0.865	1.882	0.540	0.875	2.263	1.485	0.852
Biltstar	1.089	0.888	1.690	0.558	1.015	3.038	2.414	0.662

Table 7

Zinc uptake/accumulation (mg Zn kg^{-1} d.m.; g Zn ha^{-1}) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested variant. Mean; mature plants; field-simulated experiment 2005-2007

Variety	**Root**	**Stem**	**Capsule**	**Seed**	**Root**	**Stem**	**Capsule**	**Seed**
	[mg Zn mg·kg^{-1}]				**[g Zn·ha^{-1}]**			
Hermes	34.294	36.921	135.152	71.530	36.526	192.214	98.000	55.428
Jitka	33.999	40.694	129.667	74.767	26.131	186.563	102.144	57.474
Venica	32.650	36.408	99.740	69.987	34.164	201.528	85.222	79.613
Merkur	35.134	37.249	106.248	67.710	27.776	139.086	79.856	50.648
Bonet	30.806	36.673	106.958	71.125	23.425	159.847	75.637	59.507
Tábor	31.629	37.803	118.981	73.572	27.314	194.948	96.153	69.966
Viola	39.568	37.117	113.759	70.604	33.161	191.841	86.379	54.142
Viking	33.834	35.481	104.983	71.288	32.062	172.937	110.961	58.642
Agatha	27.904	35.919	95.629	68.144	29.928	196.964	73.999	60.813
Escalina	38.104	37.651	115.926	66.891	34.197	171.101	87.882	66.153
Ilona	33.716	37.754	117.925	75.498	30.299	180.807	83.819	54.311
Super	33.841	33.071	113.186	72.918	27.123	127.095	86.779	50.431
Elektra	33.253	35.448	102.679	68.958	36.946	198.972	64.145	43.104
Marylin	33.567	41.392	128.114	76.284	36.403	217.994	108.826	66.334
Jordán	33.267	38.469	118.469	77.860	40.191	238.298	95.295	54.282
Laura	38.074	39.442	118.162	75.613	37.109	164.529	98.155	72.798
Atalante	31.946	34.034	102.243	70.049	29.886	130.248	100.939	105.443
Flanders	29.330	39.133	132.313	62.120	24.190	103.126	121.591	71.819
Lola	32.471	38.986	123.902	64.099	21.179	95.162	92.572	79.537
Biltstar	38.241	39.559	116.255	74.512	32.816	144.111	145.187	68.726

Table 8

Heavy metal (Cd, Pb, Zn) uptake/accumulation (mg Cd, Pb, Zn kg^{-1} d.m.; g Cd, Pb, Zn ha^{-1}) by organs of flax and linseed plants from sewage sludge-amended soil irrespective of tested cultivars and variant (data for 20 flax and linseed cvs. and 5 variant mixture sludge and soil). Analysis of variance; mature plants; field-simulated experiment 2005-2007

		Root	**Stem**	**Capsule**	**Seed**	**Root**	**Stem**	**Capsule**	**Seed**
		[mg·kg^{-1}]				**[g·ha^{-1}]**			
Flax	**Cd**	0.321^{a}	0.377^{a}	0.368^{a}	0.113^{a}	0.328^{a}	2.168^{a}	0.268^{a}	0.098^{a}
Linseed		0.318^{a}	0.474^{a}	0.420^{a}	0.153^{b}	0.280^{a}	2.220^{a}	0.447^{b}	0.199^{b}
Flax	**Pb**	1.141^{a}	0.867^{a}	1.918^{a}	0.542^{a}	1.099^{a}	4.405^{b}	1.467^{a}	0.542^{a}
Linseed		1.235^{a}	0.851^{a}	1.732^{a}	0.590^{a}	1.092^{a}	2.644^{a}	1.836^{b}	0.884^{b}

Flax	**Zn**	33.978[a]	37.343[a]	114.099[a]	72.047[b]	32.047[b]	183.420[b]	89.578[a]	59.603[a]
Linseed		32.997[a]	37.928[a]	118.679[a]	67.695[a]	27.018[a]	118.162[a]	115.072[b]	81.381[b]

$p \leq 0.05$ - statistical significance at a 95% level of significance. Variants with identical letters express statistically insignificant differences.

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WPŁYW APLIKACJI OSADÓW ŚCIEKOWYCH DO GLEBY NA AKUMULACJĘ Cd, Pb I Zn W LNIE ZWYCZAJNYM (*Linum usitatissimum* L.)

Abstrakt: Osad ściekowy jest produktem procesu oczyszczania ścieków. Osady ściekowe mogą być uznane za odpady niebezpieczne, wymagające kosztownych procedur usuwania lub mogą być postrzegane jako źródło składników odżywczych do stosowania na gruntach rolnych. Badania przeprowadzono w symulowanych warunkach naturalnych - w doniczkach umieszczonych w ziemi na głębokość 50 cm, zawierających mieszaninę naturalnych osadów i gleb. Osady ściekowe dodano do odważonej ilość gleby w proporcjach: osady - gleba = 1:2 (var. K1), 1:3 (var. K2), 1:4 (var. K3), 1:5 (var. K4), 1:6 (var. K5). Wariant kontrolny (K0) bez obecności osadów ściekowych również obsiano wszystkimi odmianami. Badano odmiany lnu włóknistego i lnu oleistego. Odmiany lnu włóknistego i oleistego różnie zakumulowały zwłaszcza metale, najwyższe stężenia zanotowano dla Zn, a następnie Pb i Cd. Najniższe stężenia Cd i Pb były analizowane w materiale siewnym (0,121 $mg \cdot kg^{-1}$) a najwyższe stężenia Cd i Pb stwierdzono w łodydze (Cd = 0,396 $mg \cdot kg^{-1}$) i kapsułkach nasiennych (Pb = 1,881 $mg \cdot kg^{-1}$). Najwyższe stężenie Zn stwierdzono w kapsułkach nasiennych (115,015 $mg \cdot kg^{-1}$), a najniższe w korzeniach (33,782 $mg \cdot kg^{-1}$). Trend akumulacji Cd: łodyga > kapsułka nasienna > korzeń > nasiona, Pb: kapsułka nasienna > łodyga > korzeń > nasiona, Zn: kapsułka nasienna > nasiona > korzeń > łodyga. Wyniki badań i eksperymentów pokazują, że poszczególne odmiany lnu włóknistego i lnu oleistego wykazują zmienność umiejętności akumulacji metali ciężkich z gleby, a tym samym różne potencjały fitoremediacji.

Słowa kluczowe*: Linum usitatissimum* L., len włóknisty, len oleisty, kadm, ołów, cynk

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METHODS FOR MEASUREMENT AND VISUALIZATION OF CHANGES IN BIODIVERSITY

METODY POMIARU I WIZUALIZACJI ZMIAN BIORÓŻNORODNOŚCI

Abstract: Biodiversity can be evaluated basing on the species numbers or numbers of chosen taxa (S). The biodiversity assessment is also enabled using the Shannon index (H) that includes numbers of taxa and their relative abundances (or relative biomass likely relative degrees of covering). The proper description of biological or statistically significant differences (or their absence) between the compared taxocenosis of identical or subjectively different values of S and H, is not possible by use of both methods mentioned. Thus, the aim of our work was to present the manners for solving these problems basing on the example of three hypothetical organism communities. Two of the communities mentioned were characterized by the same values of S (taxon richness) and different values of H (the Shannon index) and two ones had similar H values and different values of S. To obtain the complete description of biological differences between compared communities the following indices were calculated: H_{max} (a maximum value of Shannon index for the richness of taxa represented by the same number of individuals), V_d (a percentage value of covering structural capacity of community, "evenness deficiency"), E (MacArthur index - a taxon number (S) in a community for which the observed value of H equals H_{max}) and P_s (taxon richness shortage in percents). Moreover, graphical method of Δ_β, profiles was used for comparing community diversities. Instead, to obtain information about statistically significant differences in biodiversity between analyzed communities, the rarefaction curves were applied. The curves are based on the zero models and the Monte Carlo method.

Keywords: biodiversity, Shannon index, rarefaction curves, profile method

While undertaking the 'strategy of protection and rational usage of biological diversity' [1], an ideal solution would be the formation of conditions enabling the 'control of strategy to be realized', where the monitoring, ie systematic measurements, would be performed, therefore the results of the measurements reliably compared. Biodiversity (biological *diversity* α, β, and γ) may be evaluated based on the *richness of species* S, or taxa selected at own preference [2]. It may also be assessed with consideration of the number of taxa and their relative abundance (or relative biomass, or relative coverage degree) by calculating *Shannon's index of diversity* H'. While applying both methods, it is not possible to determine correctly the biological or statistically significant differences (or the lack of such differences) between the compared taxocenoses of identical or subjectively different S and H' values. Hence, the objective of the presented study is to demonstrate methods of solving this problem, which can possibly be adopted.

Materials and methods

The material used for the study were three hypothetical communities, two of which had the same values S (species richness), but differed with respect to the H' values (Shannon's index), and two possessed similar H' values but differed by S values; for better illustration of the problem - they had the same number of individuals N = 20 (Tab. 1).

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Table 1

Taxonomic-biocenotic characteristics of three hypothetical communities A, B and C

Taxa	Community		
	A	B	C
s_i	n_i	n_i	n_i
a	4	10	3
b	4	1	6
c	4	3	-
d	4	2	4
e	4	4	7

The below-mentioned formulas were applied to perform measurements and comparisons of biological diversity of the communities (objects) characterised [3-5]:

$$S = \sum_{i=1}^{s} s_i \tag{1}$$

$$N = \sum_{i=1}^{S} n_i \tag{2}$$

$$\Pi_i = \frac{n_i}{N} \tag{3}$$

$$H' = -\sum_{i=1}^{S} \Pi_i \lg_2 \Pi_i \tag{4}$$

$$H'_{max} = \lg_2 S \tag{5}$$

$$V_d = \left(1 - \frac{H'}{H'_{max}}\right) \cdot 100 \tag{6}$$

$$E = 2^{H'} \tag{7}$$

$$P_s = \left(1 - \frac{E}{S}\right) \cdot 100 \tag{8}$$

where: S - species richness, number of taxa; s_i - distinguished taxon; N - total number of individuals in the sample (total number of individuals in taxocenosis); n_i - number of individuals of i^{th} taxon; Π_i - relative abundance of the i^{th} taxon; H' - Shannon's index of biodiversity; H'_{max} - maximum H' value for a given richness S, which would occur if all taxa were equally abundant; V_d - a percentage value of implementation of community capacity (evenness deficiency), E - species richness of community, for which the observed H' is H'_{max} value; P_s - expressed in percent species shortage.

Moreover, in order to compare the biodiversity of communities, a graphic profile method of Δ_β was applied [4]. The Δ_β profiles were plotted based on the points on the coordinate axes (β, Δ_β), where $\beta > -1$ and Δ_β is described by the following formula:

$$\Delta_\beta = \sum_{i=1}^{S} \left\{ \frac{1 - \Pi_i^\beta}{\beta} \right\} \Pi_i = \frac{1 - \sum_{i=1}^{S} \Pi_i^{\beta+1}}{\beta} \tag{9}$$

To obtain information concerning the statistically significant differences between the communities analysed from the aspect of diversity of the taxa, null models were applied, which are based on the Monte Carlo method [6, 7]. For the analysed communities A, B and C calculations were performed by means of the Eco Sim 7.0 software [6, 7], obtaining data necessary for plotting rarefaction curves.

Results and discussion

Table 2 presents the results of calculations performed according to the formulas (1)-(4).

Table 2

Taxa richness, total abundance and Shannon's index for communities A, B, and C

Index	Community		
	A	B	C
S	5	5	4
N	20	20	20
H'	2.3219281	1.9232196	1.9261206

Based on the above-presented results, it is not possible to state unequivocally if the communities compared, especially B and C, vary with respect to the biological differences. However, based on the data contained in Table 3, it may be presumed that in the biological sense community C is poorer with respect to biodiversity than community A, but richer than community B because it is characterised by a lower evenness deficiency V_d and a lower species shortage P_s.

Table 3

Values of indices H'_{max}, V_d, E and P_s for communities A, B and C

Index	Community		
	A	B	C
H'_{max}	2.3219281	2.3219281	2.0
V_d	0.0%	17.2%	3.7%
E	5.0	3.7926851	3.8003192
P_s	0.0%	24.2%	5%

Figure 1 present the results of the application of the profile method. It is worth explaining that Δ_β profiles plotted for compared communities show their ranking according to three indices: 'species count' $\Delta_{Si} = S - 1$, Shannon's index and Simpson's index $\Delta_{Si} = 1 - \sum_{i=1}^{s} \prod_i^2$.

For the communities considered, based on the Δ_β profiles it may be presumed that taxocenosis A is more diverse than taxocenoses B and C, while the taxocenoses B and C cannot be compared due to the crossing courses of the profiles (Fig. 1).

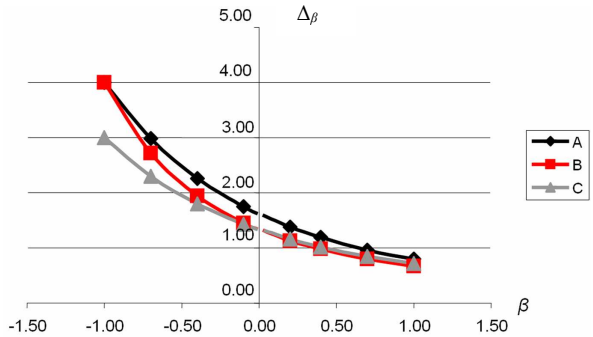

Fig. 1. The Δ_β profiles for communities A, B and C

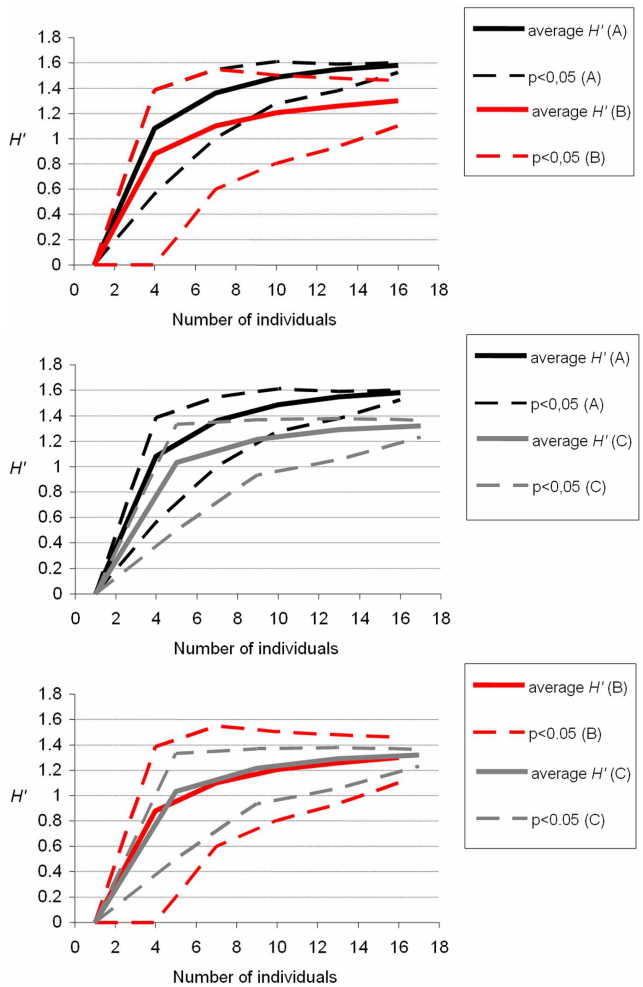

Fig. 2. Rarefaction curves of Shannon's index H' for communities A, B and C

The above-presented methods do not allow making judgements concerning neither statistical significance of the differences nor confidence intervals - the latter, when they do not overlap, decide about the significance of the differences between the communities compared. The problem discussed may be solved based on the multiple sampling methods. Using these methods, the rarefaction curves were obtained for the compared communities A, B and C (Fig. 2). A low number of taxa and individuals causes a certain 'angularity' of the graphs obtained, which should disappear with regard to more abundant samples $N > 50$.

The H' values obtained with the use of the EcoSim 7.0 software differ from those listed in Table 2, because the EcoSim software calculates Shannon's index using a natural logarithm, while the base-2 logarithm is commonly applied in the theory of computer science. Hence, H'(A) value is 1.61, and H'(B) and H' (C) obtains the value of 1.33.

The present graphs were plotted with the use of MS Excel 2007 software. The authors of the EcoSim software suggest the application of the SigmaPlot or S-Plus software, which enable more desired effects to be obtained with respect to the graphic illustration of the calculations performed [6-8]. The application of Excel also provides opportunities of interpretation of the results; therefore, based on the results, it may be presumed that in the case of Shannon's species diversity, taxocenosis A significantly differs from taxocenoses B and C, which do not differ by the parameter discussed.

Summary and conclusions

Analysis of the results allows for the following conclusions:

- Biodiversity may be expressed quantitatively, and after performing its measurements it is possible to compare taxocenoses and their changes in time function with respect to this parameter.
- The rarefaction methods enable determination of the statistical significance of the differences, or statistical lack of the differences, between Shannon's index values for the compared communities.
- Elaborate indices - derivatives of the H' index (especially V_d and P_s) allow concluding about the significance of the biological differences, even when the values of the Shannon's H' indices are numerically similar.
- The Δ_β profiles serving the comparison of the values of species richness, Shannon's and Simpson's indices in the investigated taxocenoses, have a basic shortcoming - the β values in the denominator of the fraction have to pass by 0 value, which from the point of view of arithmetic is inadmissible.

Acknowledgement

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METODY POMIARU I WIZUALIZACJI ZMIAN BIORÓŻNORODNOŚCI

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Abstrakt: Bioróżnorodność można oceniać na podstawie liczby gatunków lub liczby dowolnie wybranych taksonów (S). Ocenę bioróżnorodności można również przeprowadzić za pomocą indeksu Shannona (H), do obliczeń którego wykorzystuje się liczbę taksonów oraz ich względne liczebności (lub względne biomasy ewentualnie relatywne stopnie pokrycia). Przy użyciu obu wymienionych metod nie można poprawnie określić statystycznie istotnych czy też biologicznych różnic (lub ich braku) pomiędzy porównywanymi taksocenozami o identycznych lub subiektywnie różnych wartościach S i H. Stąd celem prezentowanej pracy było przedstawienie sposobów rozwiązania tego problemu na przykładzie trzech hipotetycznych zbiorowisk żywych organizmów. Wśród tych taksocenoz dwie charakteryzowały się takimi samymi wartościami S (bogactwa taksonów) i różnymi wartościami H (indeksu Shannona), a dwie miały zbliżone wartości H, a różne wartości S. Dla pełnego określenia różnic biologicznych pomiędzy porównywanymi zbiorowiskami obliczono wskaźniki: H_{max} (maksymalna wartość indeksu Shannona dla danego bogactwa taksonów charakteryzujących się takimi samymi liczebnościami), V_d (wyrażona w % wartość wypełnienia strukturalnych możliwości zbiorowiska; niedostatek „równomierności"), E (indeks MacArthura, czyli liczba taksonów S w zbiorowisku, dla którego dany indeks H przyjąłby wartość maksymalną) oraz P_s (wyrażony w % niedostatek bogactwa taksonów). Dodatkowo, dla porównania bioróżnorodności zbiorowisk użyto graficznej metody profili Δ_β. W celu uzyskania informacji o statystycznie istotnych różnicach między analizowanymi zbiorowiskami pod względem bioróżnorodności wykreślono krzywe rarefakcji, bazujące na modelach zerowych i metodzie Monte Carlo.

Słowa kluczowe: bioróżnorodność, indeks Shannona, krzywe rarefakcji, metoda profili

Renata GNATOWSKA[1]

NUMERICAL MODELING OF POLLUTANT DISPERSION IN FLOW AROUND THE OBJECTS IN TANDEM ARRANGEMENT

NUMERYCZNE MODELOWANIE ROZPRZESTRZENIANIA SIĘ ZANIECZYSZCZEŃ GAZOWYCH WOKÓŁ OBIEKTÓW W KONFIGURACJI TANDEM

Abstract: The dispersion of pollutants in space around wind engineering structures governed by convection and diffusion mechanism and depends strongly on the velocity field. To understand the phenomena related to the forming of concentration fields it is necessary to recognize the local features of the flow around the objects with the special emphasize for the mean velocity direction, random and periodical fluctuations accompanying the vortex generation in bodies neighbourhood. The specific flow conditions generated around bluff bodies arrangement make it possible to study the gas pollutant dispersion for the case of very complex velocity field typical for built environment. The paper presents the results of the complex research program aimed at understanding a character of the flow field in neighborhood of bluff-bodies immersed in a boundary layer and characteristics of pollutants dispersion in that area. The analysis has been performed for the 3D case of two surface-mounted bluff bodies arranged in tandem. The local characteristics of flow and concentration profiles of tracer gas (CO_2) for various inter obstacle gaps were obtained by the use of commercial CFD code (FLUENT). Characteristic feature of flow field around groups of buildings in urban areas is high level the unsteady phenomena resulting from itself character of the wind or from the interference of the wake flow connected with a process of vortex shedding. This is the factor affecting process of the dispersion of pollutants in the built-up area acting more complex the mechanism of propagate of small parts explained on the basis of processes of advection and turbulent diffusion.

Keywords: numerical modelling of pollutant dispersion, buildings arrays

The analysis of pollutant dispersion throughout atmospheric boundary layer has grown in importance since human activity has become so intense that it started having considerable impact on natural environment. The level of concentration of pollutants has grew, particularly in urban areas and it impacts on their inhabitants.

Ensuring adequate air quality requires proper aeration of these areas. Its efficiency depends mainly on arrangements of the buildings, the wind direction and locations of emissions sources. The process of pollution dispersion is mainly influenced by mechanisms of mass diffusion, caused by concentration gradients and advection which transfers pollutants in flow direction through mean air movement. Another important factor affecting the entrainment of pollutants into and out of the wake region is the unsteadiness of the wake caused by the shedding of corner vortices. Important role is also played by turbulent transport processes [1, 2]. Improvement in air quality on a local scale and limitation of effect of pollution on human health requires consideration of all the listed factors.

With a steady growth in computer technology, the *computational fluid dynamics* (CFD) has emerged as an effective tool to establish better understanding of the wind flow and dispersion processes that occur in the atmospheric boundary layer. The study of pollution entrainment in urban areas with different arrangements of bluff bodies is a new stem of environmental engineering. Since the analysis of flow field in complex geometries

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is very costly, the simple pollution dispersion around a cubes mounted on a surface is still under investigation.

This paper presents the numerical tests of the qualification of the relation between a structure of the flow field in complex urban terrain (in the built-up area) and characteristics of pollutants dispersion. The numerical results are compared with experimental data presented in previous article [3]. The aim of this work was to determine the impact of objects configuration, their degree of "immersion" in the boundary layer for the spread of the tracer gas emitted in the vicinity of two rectangular blocks in tandem arrangement.

Methods of analysis

The program of this work consists of comparison of pollutant concentration profiles with aerodynamic characteristics for building-downwash effect (obtained as a result of numerical simulation).

The geometries of the analyzed cases of two obstacles and location of the source in relation to the investigated arrangement of the objects as well as the assumed coordinate system are presented in Figure 1. The three-dimensional CFD domain consisted of two objects with a square base (0.04 x 0.04 m) and different heights. The total height, width and length of the domain was accordingly 10 x 10D and 30D. The inflow boundary layer has been prescribed according to the power law distribution $U(z) = U_\delta(z/\delta)^\alpha$, where α characterizes the terrain type.

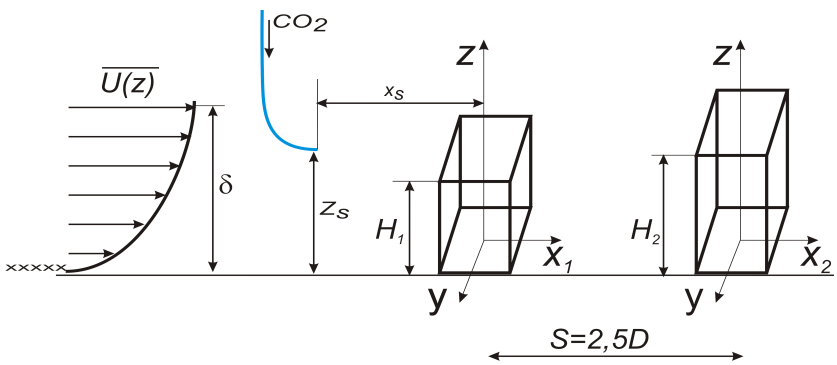

Fig. 1. Schematic diagram of objects in tandem arrangement used in the numerical simulations and nomenclature

All the measurements were carried out for the Reynolds number $Re_D = 3.4 \cdot 10^4$ based on the free stream velocity $U_\infty = 13$ m/s. The source of emission of carbon dioxide used as a gas marker during the investigations was a pipe located on the symmetry line of the objects at the distance of $x_s = -2.5D$ and at the height $z_s = H_1$ before the windward one. The CO_2 emission rate was assumed $Q = 5$ dm^3/min.

The results of study presented in this work relate to a fixed ratio of object height $H_1/H_2 = 0.6$ and their "immersion" in boundary layer $H_2/\delta = 0.6$.

Three-dimensional RANS simulations have been carried out using a commercial CFD code, FLUENT v.6.2, with the RNG version of a k-ε turbulence. According to the literature [4, 5] this model is widely used for flows in a build environment. For the considered

configuration the experimental verification of numerical data has been performed in wind tunnel, which details and results were presented in previous article [3].

Discussion of the results

The analysis of gas pollutants dispersion process requires in-depth identification of the structure of flow around the buildings. The flow structure around three-dimensional bluff-body located on the surface with formed boundary layer is characterized by a high level of complexity.

The case under consideration in this work concerns tandem arrangement which is characterized by H_1/H_2 parameter, which is conducive to occurrence of so-called "downwash" effect $H_1/H_2 = 0.6$. This effect consists in washing of front side of the leeward object with large air masses, which results in strong air circulation in the area between objects, which determines flow structure between them. The zone typical of flow between cuboids are clearly visible in the image (see Fig. 2a) being the result of smoke visualization The level of modification of flow around the analysed arrangement of objects of tandem type depends on many factors (distance between elements, change in height of the objects, immersion parameter in boundary layer). Figure 2b presents distribution of concentration field in flow around the elements for the source located at the height of the windward object. The results show that the biggest changes in flow field are observed in the area between objects.

The smoke vortex flow visualization (experimental measurements) and concentration contour plots (numerical calculations) are clearly reflected the qualitative nature of the flow in the area between the buildings (see Fig. 2ab). The observed modifying impact of interaction between the objects in tandem arrangement is reflected in the results of concentration of the tracer gas emitted in their environment.

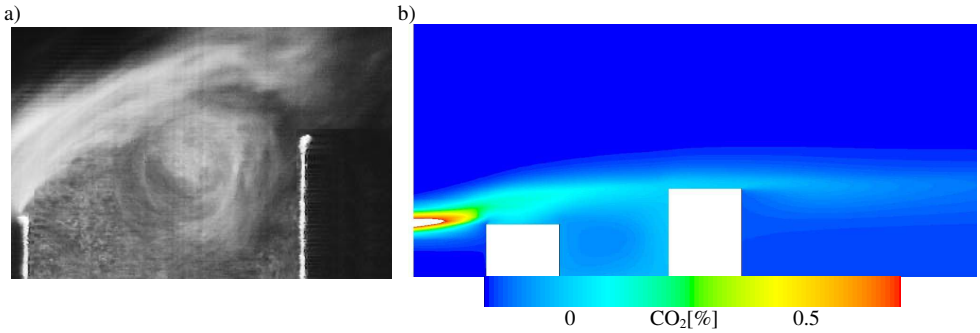

Fig. 2. The flow patterns obtained with smoke visualization technique - results of wind-tunnel experiments (a), The CO_2 concentration contour plots at plane y/D = 0 for considered configuration objects in tandem arrangement - results of numerical calculations (b)

In the case of the tandem arrangement, being considered here, in addition with "downwash" effect the arrangement low-height elements can contribute to the intensification of mixing processes and consequently lead to improved air quality at the zone between objects as it was pointed out by Vanweert & van Rooij [6]. Appropriate

design of the wind environment with the presence of emission sources is very important especially taking into account human health and life comfort.

Disturbing impact of the second object on the flow around the analysed arrangement of cubes causes many changes. This is illustrated by Figure 3 which shows the cross-sectional distribution of CO_2 concentration in and behind the objects gap for the considered configuration. The general behavior of the concentration field is similar to obtain in experimental measurement. It can be seen the high value of the gas marker concentration, emitted at the height of the windward object, at a certain distance from the source and a decrease along the flow direction. The gas marker is moved mainly through upper flow. The pollutant plume width predicted at the pedestrian level and at the ground level in gap between objects is wider than in other part of gap flow. When the CO_2 plume arrives to front side of the leeward object, which results the strong value of concentration in that area. The images that we can observed between objects are the result of the flow structure between them. This situation is confirmed in Figure 3 (see $x_2/D = 0.5$), which shows the lower values of pollutant concentration behind the array of two cuboids. It is caused by the recirculation bubble in the gap region between objects in tandem.

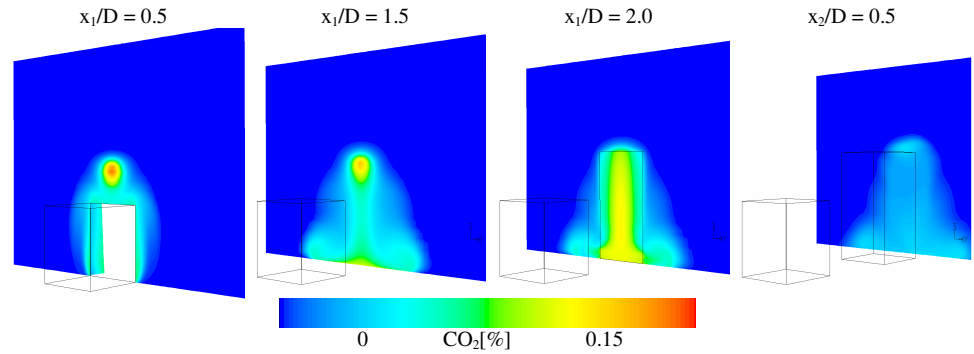

Fig. 3. The CO_2 concentration contour plots at various planes x/D = const for considered configuration objects in tandem arrangement - results of numerical calculations

The differences appear practically for each location of the source and each measuring traverse. The highest values of marker gas in tandem arrangement axis (y/D = 0) are observed for $z_S = H_1$ in the area above the height of windward building, while for the source located on the base, along almost the whole height of the first element. For $z_S = H_1$ the values of gas marker concentration are almost ten times bigger for y/D = 0 than y/D = 0.5 while for $z_S = 0$ the situation is opposite (twice the difference). In the case of the measurements along the outside edges (y/D = 0.5), maximal C_{CO2} values appear in the base.

Conclusions

The performed numerical research was aimed primarily at the development of the existing knowledge of the interaction between objects located on the ground and its influence on the pollutant dispersion. Such studies may contribute to the better understanding of physical processes and provide necessary information for the development of numerical modeling.

In present experimental study of CO_2 concentration fields around bluff-bodies in tandem arrangement have been observed for case so-called "downwash" effect $H_1/H_2 = 0.6$. The main attention of this paper was to determine the impact of objects configuration, their degree of "immersion" in the boundary layer for the spread of the tracer gas emitted in the vicinity of two rectangular cubes in tandem arrangement.

The presented results show how important for ensuring adequate air quality, human health and their wind comfort, proper formation of wind-related environment of ground objects is.

Acknowledgements

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NUMERYCZNE MODELOWANIE ROZPRZESTRZENIANIA SIĘ ZANIECZYSZCZEŃ GAZOWYCH WOKÓŁ OBIEKTÓW W KONFIGURACJI TANDEM

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Abstrakt: Rozprzestrzenianie się zanieczyszczeń w przyziemnej warstwie atmosferycznej regulowane jest przez mechanizmy dyfuzji i konwekcji oraz silnie zależy od pola prędkości. W celu zrozumienia zjawisk związanych z kształtowaniem się pól koncentracji istotne jest rozpoznanie struktury przepływu wokół obiektów ze szczególnym uwzględnieniem prędkości średniej oraz jej losowej i okresowej składowej towarzyszącym generacji wirów w otoczeniu obiektów naziemnych w obszarach zabudowanych. W pracy przedstawiono wyniki numerycznego modelowania procesu dyspersji zanieczyszczeń gazowych w strefie zabudowanej. Ich celem było określenie wpływu konfiguracji obiektów, stopnia ich „zanurzenia" w warstwie przyziemnej, a także położenia źródła emisji na rozprzestrzenianie się zanieczyszczeń (znacznik gazowy - CO_2). Badany układ stanowiły dwa trójwymiarowe modele budynków o różnych wysokościach ustawione w tandemie. Charakterystyki aerodynamiczne przepływu oraz profile koncentracji gazu znacznikowego (CO_2) dla różnych konfiguracji obiektów uzyskano z wykorzystaniem komercyjnego oprogramowania FLUENT. Cechą szczególną pól prędkości w otoczeniu grupy opływanych budynków jest wysoki poziom niestacjonarności wynikający zarówno z samego charakteru wiatru, jak i z faktu generowania przez obiekty zjawisk periodycznych związanych z procesem schodzenia wirów. Jest to czynnik, który oddziałuje na proces dyspersji zanieczyszczeń w obszarze zabudowanym, czyniąc jeszcze bardziej złożonym mechanizm rozprzestrzeniania się cząstek, tłumaczony za pomocą procesów adwekcji i turbulentnej dyfuzji.

Słowa kluczowe: numeryczne modelowanie dyspersji zanieczyszczeń, układy budynków

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Andrzej ŻARCZYŃSKI[1], Tadeusz PARYJCZAK[1], Adam KĘDZIORA[1]
Radosław CIESIELSKI[1] and Monika PISAREK[1]

DETERMINATION OF AMMONIA AND OTHER POLLUTANTS IN AIR AND IN THE AREA OF POULTRY KEEPING FARMS

OZNACZANIE AMONIAKU I INNYCH ZANIECZYSZCZEŃ NA TERENIE FERMY HODOWLI DROBIU

Abstract: Polluted air in a big farm of poultry keeping (~18 thousands of chickens) in Lodz province was sampled. The aim of the investigation was to determine odour pollutants, especially ammonia, in air and check the possibility of a catalytic method application in their removal. Gas samples were analyzed on the spot of sampling with an application of gases analyser Madur GA-20, as well as in a laboratory with an application of instrument and spectrophotometric methods. The intensity of odours was estimated using five-stage scale applied by local authorities in Japan for odorous protection of air quality. Within sampling period, poultry keeping in the farm was the source of variable in time ammonia emission ranging from 0.82 to 2.65 mg/m^3. Air inside in farm contained carbon dioxide (0÷0.3%) and oxygen (20.5÷20.9%). Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m^3) and formaldehyde (> 0.25 mg/m^3) was not detected. The highest odour intensity inside the building of chicken keeping and at outlets of ventilators was at the third stage in odour scale applied in Japan (3.5), ie, clearly perceptible. However, it decreased significantly with the increase in a distance from the building.

Keywords: chicken farms, ammonia determination, odours in agricultural production

Poultry keeping farms, are the biggest sources emitting pollutants of all types, ie chemical - gases, mechanical - dusts and biological - microorganisms. Ammonia is the most noxious gas for the environment, produced by poultry keeping farms. Gases removed by ventilation contain also dimethylamine, carbon monoxide and dioxide, aldehydes, ketones, organic acids and many other organic compounds belonging to odours [1-5].

Ammonia is generated in poultry houses as a by-product during microbiological decomposition of organic compounds containing nitrogen in droppings and residual feed. The decomposition proceeds enzymaticly or with the participation of anaerobic bacteria [5-7]. The most important aim in the limitation of ammonia emission is maintenance of hygiene at the high level in the poultry house as well as equipment of efficient ventilation system. Well designed ventilation system prevents concentration of gases in the building and keeps temperature and humidity at the level which guarantees good mood and health of birds [5].

Experimental

Polluted air in a big farm of poultry keeping (~ 18 thousands of chickens) in the Lodz province was sampled. The aim of the investigation was to determine odour pollutants, especially ammonia, in air and check the possibility of a catalytic method application in their removal [1-3, 5]. Contents analysis of the gases carried away from their emission sources and estimation of their odour is a difficult task but possible to perform with the

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application of various methods of odour detection and odour level estimation [1, 4]. Gases sampling was carried out in the central part of the building (Fig. 1) and near outlets of ventilators at the height of 0.5 m [3, 8], in the period of poultry fattening - 5th and 6th week of the keeping, at various daytimes and seasons.

Fig. 1. Poultry house inside

Table 1

A dependence of odour intensity on concentration of selected odours applied by local authorities in Japan during determination of the highest allowable concentrations [1]

Odour intensity		**Odour concentration**				
		[ppm]				**[mg/m^3]**
		Methanethiol CH_3SH	**Acetaldehyde CH_3CHO**	**Styrene $C_6H_5CHCH_2$**	**Ammonia NH_3**	**Ammonia NH_3**
1	Detection threshold	0.0001	0.002	0.03	0.1	0.07
2	Recognition threshold	0.0007	0.01	0.2	0.5	0.36
2.5	Clear	0.002	0.05	0.4	1	0.71
3.0		0.004	0.1	0.8	2	1.42
3.5		0.01	0.5	2	5	3.55
4	Strong	0.03	1	4	10	7.10
5	Extreme strong	0.2	10	20	40	28.4

Gas samples were analyzed on the spot of sampling with an application of gases analyser Madur GA-20, as well as in a laboratory with an application of spectrophotometric methods and gas chromatography (GC-MS). Colorimetric or spectrophotometric analyses included the determination of ammonia [9, 10], hydrogen sulphide [11] and formaldehyde [12]. The intensity of odours was estimated using five-stage scale applied by local authorities in Japan for odorous protection of air quality. Table 1 presents concentration values of 4 among 8 obligatory air pollutants (ammonia, methanethiol, hydrogen sulphide,

dimethyl disulfide, trimethylamine, acetaldehyde and styrene), which determine potential harmfulness on five-stage scale applied by local authorities in Japan for determination of the highest allowable concentrations of odours in the environment [1]. The intensity of odour in air in work-places, as well as in air outside production buildings should not be higher than 3.5 stage (for ammonia 3.55 mg/m^3) which is the upper level (clear) of this stage.

Results and disscussion

Selected results of the pollutants investigation in air from the poultry keeping farm (poultry house) are presented in Tables 2-4.

Table 2

Analysis results of air sampled in a large building of the poultry keeping farm

Analysed component	Measurements - 24.09.2009 (midday). Air temperature inside the building 24ºC and outside the building 19ºC		Measurements - 01.10.2010 (evening). Air temperature inside the building 22ºC and outside the building 9ºC	
	Air in the central part of the building at the height of 0.5 m	Air at the outlet of a ventilator	Air in the central part of the building at the height of 0.5 m	Air at the outlet of a ventilator
O_2 [%]	20.5	20.9	20.9	20.9
CO_2 [%]	0.3	0	0	0
CO [ppm]	0	0	0	0
NH_3 [mg/m^3]	1.45÷2.59	N.d.*	0.82÷1.37	N.d.
Formaldehyde [mg/m^3]	< 0.25	< 0.25	< 0.25	< 0.25
Odour intensity: stage; description	3.0; clear	3.5; clear	2.5; clear	3.0; clear

* N.d. - not determined

Table 3

Analysis results of air sampled inside the poultry house on November 30, 2009 (midday). Air temperature in the poultry house 22ºC and outside 6ºC

Analysed component	Air in the central part of the building at the height of 0.5 m	Air at the outlet of a ventilator	Air in a distance of 10 m from the outlet of a ventilator
O_2 [%]	20.5	20.5	20.9
CO_2 [%]	0.3	0.3	0
CO [ppm]	0	0	0
SO_2 [ppm]	0	0	0
TOC in a solution in a gas washer [mg C/dm^3]	2.493	-	-
NH_3 [mg/m^3]	1.97÷2.65	N.d.	N.d.
Formaldehyde [mg/m^3]	N.d.	< 0.25	N.d.
Hydrogen sulphide [mg/m^3]	N.d.	< 2.0	N.d.
Odour intensity: stage; description	-	3.5; clear	2.0÷2.5; recognition threshold - clear

The presence of ammonia was found inside the poultry house at varying concentrations in the range from 0.82 to 2.65 mg/m^3 (Tables 2-4). Results of the analyses show that the ammonia concentration inside the building was a little bit higher at noon and in the

evening. The ammonia concentration was only 0.26 mg/m^3 (Table 4) in the air removed from the poultry house by the outlet of the side ventilator. Chromatographic analyses in the GC-MS system did not show ammonia content higher than 0.1% or organic compounds concentrations higher than 1 mg/m^3 possible for the detection in this system. Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m^3) and formaldehyde (> 0.25 mg/m^3) was not detected. Traces of dust (not detected) arising from the building and covering ventilators casing or plants below their outlets, were observed.

Table 4

Analysis results of air from the poultry keeping farm on May 25, 2010 (morning). Air temperature inside the building 22°C and outside 20°C [3]

Analysed component	**Air sampled inside the poultry house at the height of 0.5 m from the ground**	**Air removed from the inside of the poultry house and sampled at the side ventilator outlet**
O_2 [%]	20.9	20.9
CO_2 [%]	0	0
CO [ppm]	0	0
SO_2 [ppm]	0	0
CH_4 [ppm]	1.0	0
NH_3 [mg/m^3]	0.84÷1.19	0.26
Formaldehyde [mg/m^3]	< 0.25	< 0.25
Hydrogen sulphide [mg/m^3]	< 2.0	< 2.0
Odour intensity: degree; description	3.0÷3.5; clear	2.5÷3.0; clear

Odour intensity was estimated using five-stage scale developed in Japan with the third stage splitted for three levels labelled as: 2.5, 3.0 and 3.5 (clear). The measurements proved that odour intensity in the air inside the poultry house and removed by the ventillators was the highest in the third stage, ie, clear, and reached the value of, 3.5. The odour intensity decreased quickly with an increase in the distance from the ventilator in spite of air flow in the same direction (2÷3 m/s), because in the distance of about 10 m, this intensity was only at the level of the stage limit - recognition threshold and clear, ie 2.0÷2.5. The odour intensity was significant only in the distance of a few meters from the ventilator.

Conclusions

Within sampling period, poultry keeping in the farm was the source of variable in time ammonia emission ranging from 0.82 to 2.65 mg/m^3. Air inside in farm contained carbon dioxide (0÷0.3%) and oxygen (20.5÷20.9%). Concentrations of ammonia determined in the poultry house in the evening were lower than in the morning and at noon. Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m^3) and formaldehyde (> 0.25 mg/m^3) was not detected. The highest odour intensity inside the building of chicken keeping and at outlets of ventilators was at the third stage in odour scale applied in Japan (3.5), ie, clearly perceptible. However, it decreased significantly with the increase in a distance from the building.

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OZNACZANIE AMONIAKU I INNYCH ZANIECZYSZCZEŃ NA TERENIE FERMY HODOWLI DROBIU

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Abstrakt: Próbki zanieczyszczonego powietrza z dużej fermy drobiu rzeźnego (~18 tys. kurcząt) pobrano w województwie łódzkim. Celem badań było wykonanie analiz powietrza na zawartość zanieczyszczeń odorowych, zwłaszcza amoniaku, a w perspektywie zbadanie możliwości zastosowania metody katalitycznego utleniania do ich usuwania. Próbki gazów były analizowane na miejscu pobrania za pomocą automatycznego analizatora gazów Madur GA-20, a także w laboratorium metodami instrumentalnymi i spektrofotometrycznymi. Do oceny intensywności zapachu stosowano pięciostopniową skalę wykorzystywaną przez władze lokalne w Japonii do ochrony zapachowej jakości powietrza. Hodowla drobiu w badanej fermie była w okresie pobrania próbek źródłem zmiennej w czasie emisji amoniaku w granicach 0,82÷2,65 mg/m^3. W powietrzu obiektu stwierdzono 0÷0,3% ditlenku węgla i 20,5÷20,9% tlenu, natomiast nie wykryto tlenku węgla, ditlenku siarki, siarkowodoru (> 2,0 mg/m^3) ani formaldehydu (> 0,25 mg/m^3). Najwyższa intensywność odorowa wewnątrz budynku hodowli kurcząt, a także na wylotach wentylatorów mieściła się w trzecim stopniu skali zapachu stosowanej w Japonii (3,5), tj. wyraźny, jednak znacznie obniżała się wraz z oddalaniem się od obiektu.

Słowa kluczowe: fermy drobiu, oznaczanie amoniaku, odory w produkcji rolnej

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EFFECT OF SOIL CONTAMINATION WITH PETROL, DIESEL OIL AND ENGINE OIL ON SURVIVAL RATE OF *Arionidae* REPRESENTATIVES UNDER LABORATORY CONDITIONS

ODDZIAŁYWANIE SKAŻENIA GLEBY BENZYNĄ, OLEJEM NAPĘDOWYM I OLEJEM SILNIKOWYM NA PRZEŻYWALNOŚĆ PRZEDSTAWICIELI *Arionidae* W WARUNKACH LABORATORYJNYCH

Abstract: The investigations aimed at an assessment of representatives of *Arionidae* sensitivity to soil pollution with oil derivatives from the perspective of their use as bioindicators. The laboratory experiment, conducted in 3 replications, comprised the following objects: soil contaminated with unleaded petrol; soil contaminated with diesel oil; soil contaminated with used engine oil; control. Doses of 3,000 mg and 10,000 mg of oil derivative per 1 kg soil d.m. were applied. Petrol revealed the most toxic effect on the tested invertebrates among all three applied pollutants. Slugs revealed the greatest sensitivity only to soil contamination with petrol dose of 10,000 mg · kg^{-1} soil d.m., which evidences their considerable resistance to soil contamination with oil derivatives.

Keywords: oil derivatives, soil pollution, slugs

Gastropoda are regarded as good bioindicators of the environmental contamination [1]. Research on the effect of oil derivative effect on *Gastropoda* focused mainly on the marine environment [2, 3]. *Gastropoda* were also indicated by some authors as possible bioindicators of soil pollution with heavy metals (Cu, Ni and Co), since they were trapped exclusively in the unpolluted soil [4].

The investigations aimed at an assessment of representatives of *Arionidae* sensitivity to soil pollution with oil derivatives from the perspective of their use as bioindicators.

Material and methods

The laboratory experiment, conducted in 3 replications, comprised the following objects:

1. Soil contaminated with unleaded petrol;
2. Soil contaminated with diesel oil;
3. Soil contaminated with used engine oil;
4. Control.

Doses of 3,000 mg (marked "I") and 10,000 mg (marked "III") of oil derivative per 1 kg soil d.m. were applied. The soil used for the experiment was degraded chernozem formed from loess, classified as the very good wheat complex and soil quality class. The soil was dried at 60ºC for 5 days in a dryer and then contaminated using a syringe with formerly calculated and precisely measured amount of oil derivatives. Slugs were gathered on 23 June 2009 in Polish Aviators' Park in Czyzyny (Krakow) and then cultured for two weeks in 500 cm^3 containers. Each container held 300 g of soil dry mass. The animals were fed with fresh leaves of lettuce or dahlia supplied to the soil surface every week or more

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frequently. Five adult specimens were put in each container. Containers were covered with gauze for good ventilation. Slugs were cultured at 20±2ºC. Each week slug weight was measured. Dead specimens were removed. If the soil in the containers dried, it was sprinkled with 20 cm^3 of distilled water. Statistical analysis comprised one-way ANOVA. Means were differentiated using LSD Fisher's test. All computations were conducted using "Statistica 8.0" programme.

Results and discussion

Petrol dose of 10,000 mg · kg^{-1} soil d.m. proved the most toxic for slugs. After one day from the beginning of the experiment all specimens in this object were dead (Fig. 1). For the first four days of culturing slug mortality rate was also significantly higher than in the control in the object with soil contaminated with petrol dose of 3,000 mg · kg^{-1} soil d.m. Soil contamination with diesel oil did not apparently affect slug viability over most of the experimental period. Only after 12 days a significant increase in these animals mortality rate was observed in the object with soil contaminated with diesel oil dosed 10,000 mg · kg^{-1} soil d.m. On the other hand, in the object where soil was contaminated with diesel oil dosed 3,000 mg · kg^{-1} soil d.m. survival rate was the highest among all objects, including the control. Soil contamination with used engine oil did not affect significantly slug mortality rate, either during the experiment duration.

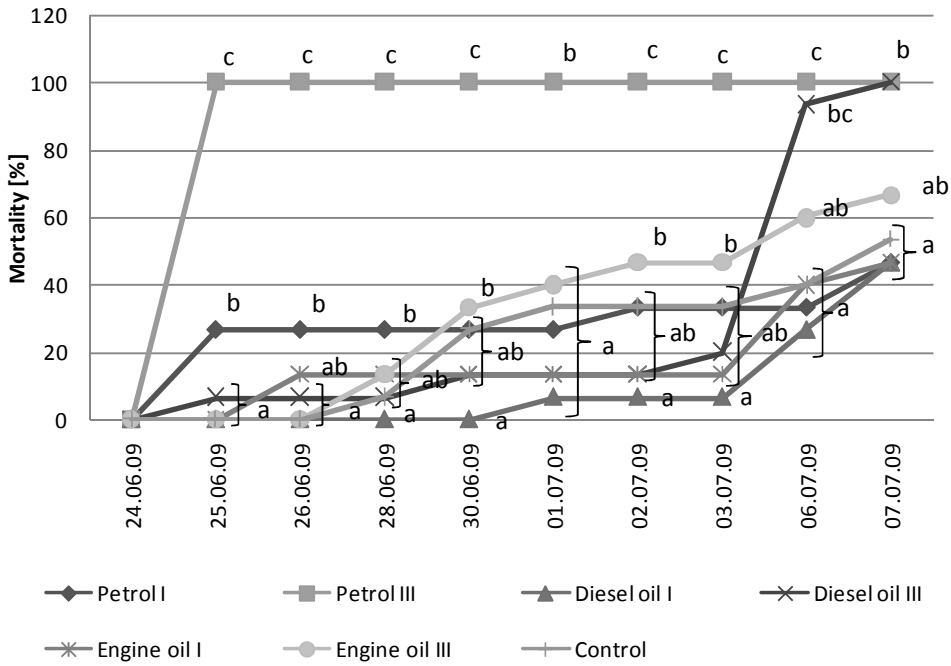

Fig. 1. Mortality rate of slugs [%] cultured in soil contaminated with oil derivatives. Means marked with different letters (a, b or c, etc) for individual dates of observation differ statistically at p = 0.05

Mean weight of live specimen during culturing was decreasing apparently in all investigated objects (Fig. 2). No statistically significant differences were noted between the analyzed objects. In long-term investigations on the occurrence of *Gastropoda* in soil contaminated with various oil derivatives the differences in the numbers of specimens trapped into pitfall traps in relation to the control were registered only after several months from the moment of soil pollution. Petrol had the least negative effect in this case, unlike under laboratory conditions. Petrol revealed the least negative effect also on the number of trapped *Hymenoptera*, *Formicidae* [5], *Coleoptera, Carabidae* [6] and *Collembola* [7]. It most probably results from its lower density and higher volatility than the other tested oil derivatives. It reveals high toxicity for a short time from the moment of pollution, which was clearly visible in the laboratory experiment. Field conditions (open space, air movement) facilitate evaporation of volatile fractions. There is a diversification between various slug species concerning their response to pollution with oil derivatives as was demonstrated by Lee et al [2] on an example of aquatic species. The authors explained the differences in sensitivity as dependant on various feeding habits. A detrivore species assimilated pollutants and was far more sensitive than herbivore species. It may also explain quite strong resistance to the applied pollutants revealed by slugs, which are herbivores, observed in the presented investigations. However, authors emphasize the advantages of slugs as indicators for testing environmental conditions, due to their abundance, ease for collection, wide distribution and sedentary nature.

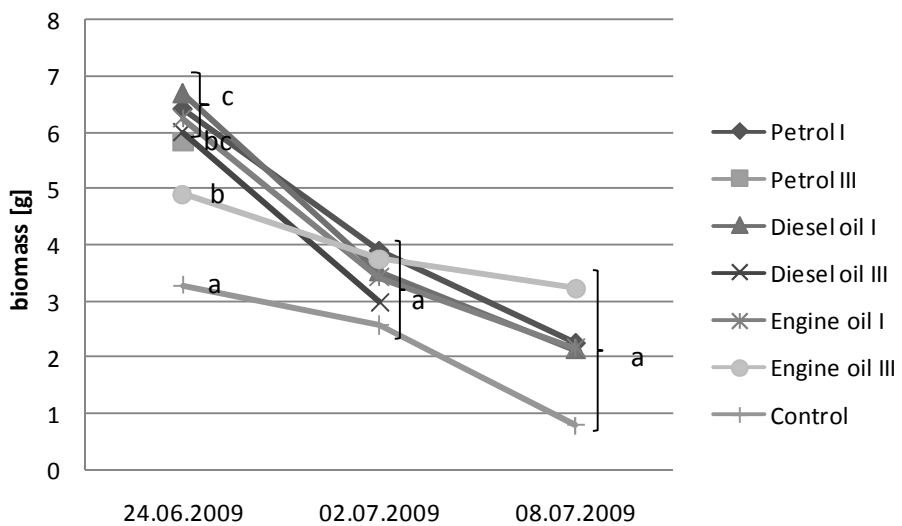

Fig. 2. Mean body weight of a single specimen of *Arionidae* cultured in soil contaminated with oil derivatives. Means marked with different letters (a, b or c, etc) for individual dates of observations differ statistically at p = 0.05

Conclusions

1. Petrol revealed the most toxic effect on the tested invertebrates among all three applied pollutants.

2. Slugs revealed the greatest sensitivity only to soil contamination with petrol dose of 10,000 mg · kg^{-1} soil d.m., which evidences their considerable resistance to soil contamination with oil derivatives.

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ODDZIAŁYWANIE SKAŻENIA GLEBY BENZYNĄ, OLEJEM NAPĘDOWYM I OLEJEM SILNIKOWYM NA PRZEŻYWALNOŚĆ PRZEDSTAWICIELI *Arionidae* W WARUNKACH LABORATORYJNYCH

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Abstrakt: Celem badań była ocena wrażliwości przedstawicieli *Arionidae* na zanieczyszczenia gleby substancjami ropopochodnymi pod kątem możliwości ich wykorzystania jako biowskaźników. Doświadczenie laboratoryjne przeprowadzono w 3 powtórzeniach i obejmowało ono następujące obiekty: gleba skażona benzyną bezołowiową, gleba skażona olejem napędowym, gleba skażona przepracowanym olejem silnikowym, kontrola. Zastosowano dawki 3000 i 10 000 mg substancji ropopochodnej na kg s.m. gleby. Benzyna charakteryzowała się najbardziej toksycznym efektem wobec badanych bezkręgowców spośród wszystkich trzech zastosowanych substancji ropopochodnych. Ślimaki wykazywały największą wrażliwość tylko na zanieczyszczenia gleby benzyną w dawce 10 000 mg · kg^{-1} s.m. gleby, co świadczy o ich dużej odporności na skażenie gleby substancjami ropopochodnymi.

Słowa kluczowe: ropopochodne, skażenie gleby, *Arionidae*

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MODIFICATION OF THE MEASUREMENT METHOD OF RELATIVE MOISTURE DETERMINATION USING PELTIER PROBE

MODYFIKACJA TECHNIKI POMIAROWEJ DO WYZNACZANIA WILGOTNOŚCI WZGLĘDNEJ ZA POMOCĄ SONDY PSYCHROMETRYCZNEJ PELTIERA

Abstract: Psychrometric probes are used for porous materials potential determination which can be easily recalculated into the relative moisture. They can be also applied for building materials moisture parameters determination. They enable relative moisture readout in the narrow range between 94 and 99.9%. Water film evaporating from the thermocouple causes temperature decrease and generation of a voltage in a range of microvolts. Due to external heat flux influence on the applied sensors (Wescor PST-55 probes) the measurement must be conducted in the stabilized conditions. Non-stable heat flows and thus the decrease of measurement results repeatability. This is especially important during measurement of porous material samples with small dimensions. To increase the measurement accuracy the probes were equipped with metal sleeves having the external diameter of 12 mm and wall thickness 1 mm. The aim of the sleeve is to stabilize the instantaneous temperature variations and bridge the heat flow around the psychrometric Peltier probe.

Keywords: psychrometric probe, sleeves

Psychrometric Peltier probe enables water potential determination in the range about –7÷–0.2 MPa which is valid for the 95÷99.9% relative moisture of the air inside pores [1]. Water potential can be described as the specific energy of bond the water in the porous material [2]. The idea of water potential and the idea of Peltier probe measurement were described in [3]. The relative humidity of air in material pores develops in equilibrium with the water in a material pores. In the equilibrium state, bond energy of water in any state, liquid or vapor, is the same, so the moisture potential of water vapor is a good measure of moisture potential of pore water. With the psychrometric Peltier probe and TDR method [4] water retention curves were determined for calcium silicate. The psychrometric probes were equipped with copper sleeves in order to diminish the influence of external heat flux onto the measurement results.

Inside the barriers made of porous building materials water can appear during building works or later during objects exploitation. Building moisture evaporates during the years and mostly it can be noticed in newly built objects.

Moisture from groundwater occurs because of the capillary rise phenomenon which relies on adsorption of water by the capillars and pores walls and depends mostly on ground conditions, capillars diameter and water chemical compound [5].

The amount of moisture which is caused by rainfalls depends mainly on capillary rise by the materials. The quicker the process the larger amount of water is absorbed comparing with water falling by the walls surface.

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Water vapor absorption from the external air by the dried material with hydrophilic properties is called moisture sorption. Moisture sorption strongly influences building barriers moisture and the materials which form them. Due to materials sorption they always contain some moisture even if not used in barriers, but only stored in the magazines.

Building barriers can also be moistened by the water vapor condensation on the surface or the internal layers. Surface condensation occurs when the air flowing close to cold surface is cooled below the dewpoint temperature and water condenses. Such a condensed water causes moisture entering the barrier material in the form of capillary water [6].

Reasons of high water content

Among the building materials threats due to water presence we can distinguish the following items:

- Physical: temperature changes and insulation parameters decrease, heat loses, scratches, material changes, wet barriers surfaces, destruction due to congealing;
- Chemical: salinity splashes, material destruction due to volume increase, structure changes, glue chemical reactions, calcium loses, rust splashes, chemical corrosion [7];
- Biological: microorganisms development, algae, moss, lichens, biocides, fungi and mould development, pollution [8].

Scheme of measurement installation

Voltage readouts from psychrometric probes PST-55 is measured by multimeter PS/1, which enables voltage measurements with the sensitivity of several microvolts [9]. Together with water potential measurement, TDR moisture measurements were done with the application of two-rod sensor and the MTS-1 measuring device (Fig. 1). Measuring device is controlled by the computer program which enables readouts synchronization. For the experiment 8 silicate samples were used with the following dimensions: 5×5×13 cm. In each sample a central hole was drilled which was used as a place to install the psychrometric probe and from the other side the TDR probes were mounted.

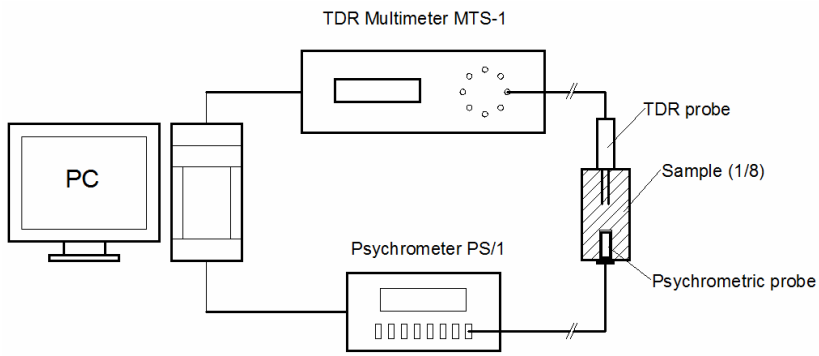

Fig. 1. Scheme of measurement installation

Psychrometric probes were placed in copper sleeves with the diameter of 10 mm and 30 mm long to stabilize heat parameters during measurement (Fig. 2). The aim of the sleeve

was to equal the heat flow q results caused by the small sample walls temperature. It is mainly caused by the different exposition of radiation.

Fig. 2. Psychrometric probe with copper sleeve

Materials and methods

Measurement of water potential was released on the samples of autoclaved calcium silicate. It is the mineral material with microporous solid phase. Billions of micro-pores are joined together and with the external air which enables high capillary parameters. This is a material enabling flow of water vapor, insulating and natural environment friendly, non flammable and preventing mould development.

Small dimensions of samples allowed to obtain a homogenous moisture in the whole volume of the sample. The process of moisturizing was released by putting the sample into the water until the maximum water content was achieved, which was determined using the TDR sensors. After this stage, psychrometric probes were mounted and the holes were insulated. Then the samples were under the process of desorption which was monitored using the measurement equipment. The first experiment series were conducted with the psychrometric probes without sleeves. In the second series the probes were armed with extra copper sleeves. Uncovered silicate samples were threatened with external parameters like daily temperature fluctuations, infrared radiation from the stuff and electrical devices. It was to compare two measurement techniques. The point of the experiment finish was constant water content value showed by the TDR device. With this information the stable state of moisture was noticed and the measurements were finished.

Results

From the diagrams presented in Figure 3 it can be concluded that the application of a copper sleeve for water potential determination using psychrometric probe positively influenced the readouts. Dispersion of measuring points was smaller which is mainly visible in the confidence band 95%. This makes the readouts more precise. This comparison is presented in Table 1. The average confidence band for measurements without sleeves was 2.0 and with the sleeves - 1.33. The copper sleeve increases the heat inertia of the direct probe environment and absorbs flowing heat which would flow through the probe. On the diagram it can be also observed the influence of daily fluctuations of external conditions where the samples were placed.

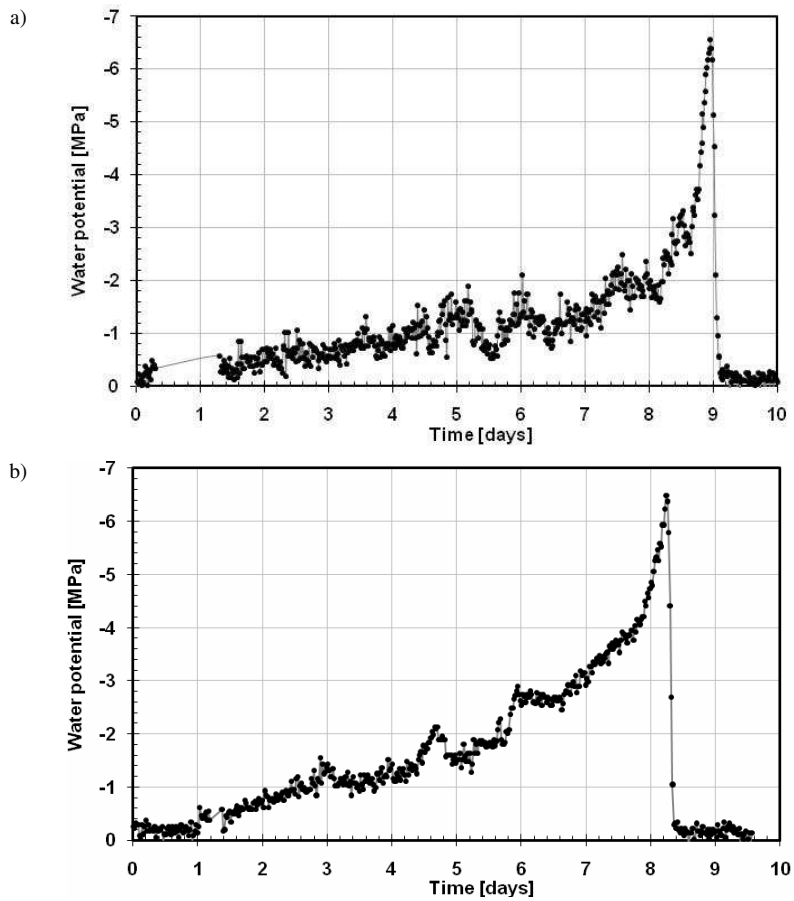

Fig. 3. Water potential in samples measured with psychrometric probes measurements: a) without sleeves, b) with sleeves

Table 1

Confidence band (0.95) of results of psychrometric probe with and without sleeve

Probe number	**1**		**2**		**3**		**4**	
Confidence band [MPa]	With sleeve	Without sleeve	With sleeve	Without sleeve	With sleeve	Without sleeve	With sleeve	Without sleeve
	1.0	1.7	1.1	1.6	1.4	2.3	1.2	2.1
Probe number	**5**		**6**		**7**		**8**	
Confidence band [MPa]	With sleeve	Without sleeve	With sleeve	Without sleeve	With sleeve	Without sleeve	With sleeve	Without sleeve
	2.5	3.0	1.1	1.3	1.0	2.1	1.3	1.9

Combining the above-presented results with the TDR probes readouts the water retention curves were elaborated in the range between –1 and –7 MPa of water potential (Fig. 4).

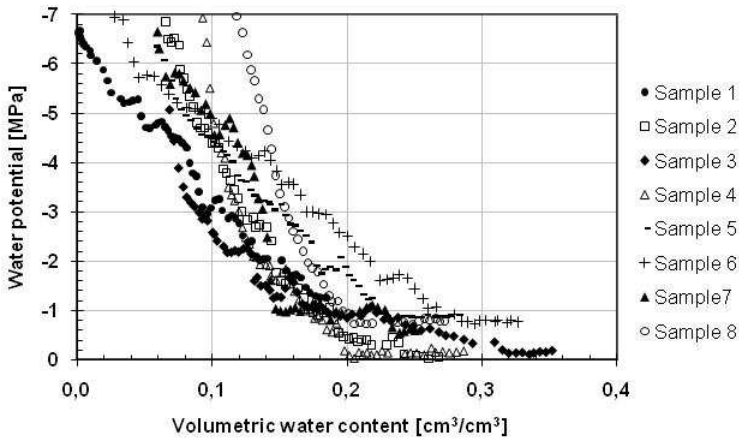

Fig. 4. Water retention curve determined through conjugation of psychrometric and TDR technique

Conclusions

Applied copper sleeves for psychrometric probes cause that in laboratory conditions the readouts are more stable which enables more precise elaboration of water retention curves of building materials.

Water retention curve elaborated with the combined TDR and psychrometric probe enables determination of pF curves in the range –1÷–7MPa, which is caused by the psychrometric probe sensivity.

Acknowledgment

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MODYFIKACJA TECHNIKI POMIAROWEJ DO WYZNACZANIA WILGOTNOŚCI WZGLĘDNEJ ZA POMOCĄ SONDY PSYCHROMETRYCZNEJ PELTIERA

Wydział Inżynierii Środowiska, Politechnika Lubelska

Abstrakt: Sondy psychrometryczne służą do pomiaru potencjału wody materiałów porowatych, którą można przeliczyć na wilgotność względną. Stosowane są od lat w agrotechnice i mogą również być zastosowane do pomiarów parametrów wilgotnościowych materiałów budowlanych. Umożliwiają odczyt wilgotności względnej w wąskim zakresie około 94÷99,9%. Jest to możliwe dzięki zjawisku Seebecka, odparowujący film wody z termopary powoduje obniżenie jej temperatury i wygenerowanie mikrowoltowego napięcia. Z uwagi na niską wartość mikrowoltowego napięcia generowanego na sondach Wescor PST-55, użytych podczas badań, pomiary muszą odbywać się w ustabilizowanych warunkach. Nieustabilizowane przepływy strumienia ciepła lub skoki temperatury powodują zmniejszenie powtarzalności wyników pomiarów. Ma to szczególne znaczenie podczas pomiarów próbek materiałów porowatych o niewielkich wymiarach geometrycznych. W celu zwiększenia dokładności pomiarów sondy zostały osłonięte metalowymi tulejami o średnicy 10 mm i grubości ścianki 1 mm. Zadaniem takiej tulei jest stabilizowanie nagłych wahań temperatury i regulowanie przepływów strumienia ciepła wokół sondy psychrometrycznej Peltiera.

Słowa kluczowe: sondy psychrometryczne, tuleje

Zdenek HAVLICEK[1] and Petr SLAMA[1]

EFFECT OF HEAT STRESS ON BIOCHEMICAL PARAMETERS OF HENS

WPŁYW STRESU CIEPLNEGO NA PARAMETRY BIOCHEMICZNE BADANYCH KUR

Abstract: The objective of this paper was to evaluate the effects of high temperatures on biochemical parameters of hens. Heat stress generally causes a decrease in feed intake. The hypothesis that feed intake, egg production, egg quality measures, acid-base status (pH, pCO_2, HCO_3^-) of hens would be influenced by the high temperature period was tested. Twenty four Isa Brown hens at 60 weeks of age were used in this experiment and hens were randomly separated into 2 equal groups. Each group contains 12 hens. First control group was housed at 20.1÷21.2°C and 60÷65% relative humidity. Experimental group was housed for 2 weeks at 20.5°C and 60÷65% relative humidity in experimental box, and then exposed to 27°C and 60% for 4 week, and then allowed to recover for 2 week at 20.5°C and 60% relative humidity. All production parameters and egg quality were significantly affected by heat stress. Feed intake during first week heat period was significantly reduced (18%). In three next weeks, feed intake was increasing with reduction 14.5%, 8% and 9.5%, respectively. Blood pH values were significantly lower from 3rd week of exposure. Blood pH had these values: 1st week 7.372, 2nd week 7.371, 3rd week 7.380 and 4th week 7.289.

Keywords: heat stress, temperature, hen, acid-base, pH

High ambient temperature is of great concern in all types of poultry operations. Heat loss in poultry is limited due to feathering and the absence of sweat glands. When the temperature and relative humidity exceed the comfort level of a bird, it loses the ability to efficiency dissipate heat. High ambient temperatures compromise performance and productivity through reducing feed intake and decreasing nutrient utilization, growth rate and egg quality, which lead to economic losses in poultry [1]. Heat stress is well known to reduce the reproductive performance of laying hens by interrupting egg production, an effect caused by a reduction in feed intake [2]. In addition, heat stress negatively affects the strength, weight, thickness and ash content of eggshell [3], as responses involve various aspect of calcium metabolism, including a reduction in free ionized calcium in the blood [4]. Hens exhibit a variety of panting patterns to lose heat as water vapor [5]. The increase in respiration rate leads to a reduction in blood partial pressure of CO_2, HCO_3^- and an increase in blood pH, resulting in respiratory alkalosis [6, 7].

Materials and methods

Twenty four Isa Brown hens at 60 weeks of age were used in this experiment and hens were randomly separated into 2 equal groups. Each group contains 12 hens. First control group was housed at 20.1÷21.2°C and 60÷65% relative humidity. Experimental group was housed for 2 weeks at 20.5°C and 60÷65% relative humidity in experimental box, and then exposed to 27°C and 60% for 4 week, and then allowed to recover for 2 week at 20.5°C and 60% relative humidity.

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Blood (4 cm^3) was drawn from the brachial vein into a syringe containing lithium heparin. All samples were stored in ice until analysed. The partial pressure of CO (pCO_2), concentration of bicarbonate ions and pH of blood and shell-gland fluid, corrected to body temperature of 41°C, were measured within 1.5 h using an acid-base laboratory OPTI Critical Care Analyzer.

The sampling intervals and measured parameters in this study are summarized in Table 1.

Table 1

Summary of measurements taken, sampling intervals used

Collection interval	Parameter
Daily	Egg production [%]
	Feed intake [g]
Once a 5 day	Acid-base status
	pH
	pCO_2
	HCO_3^-

Results and discussion

The effects of heat stress are presented in Figures 1 and 2. The statistical analysis of the present study revealed that chronic high temperature 27°C significantly ($p < 0.05$) decreased feed intake during the first seven days of the heat stress (18%). In two next weeks, feed intake was increasing with reduction 14.5, 8 and 9.5%, respectively. These results are supported by the findings of Sahin et al [1].

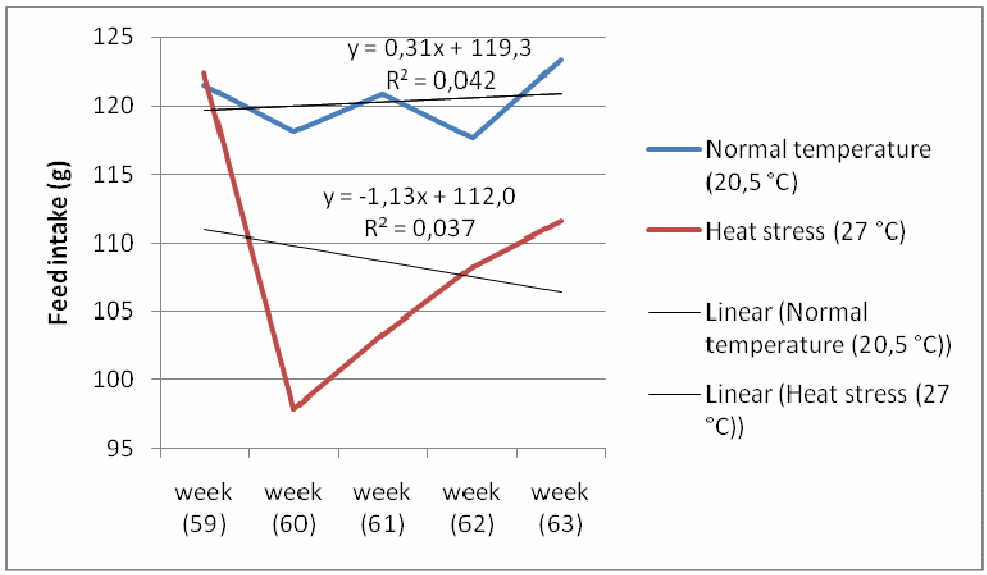

Fig. 1. Effect of heat stress on feed intake

Effect of high temperature on production is shown in Table 2. A significantly lower egg-laying was detected in the second and fourth week of heat stress exposure ($p < 0.01$). Significantly lower ($p < 0.05$) production was observed in the third week of high temperature. The highest decrease was recorded in the third week of high temperature.

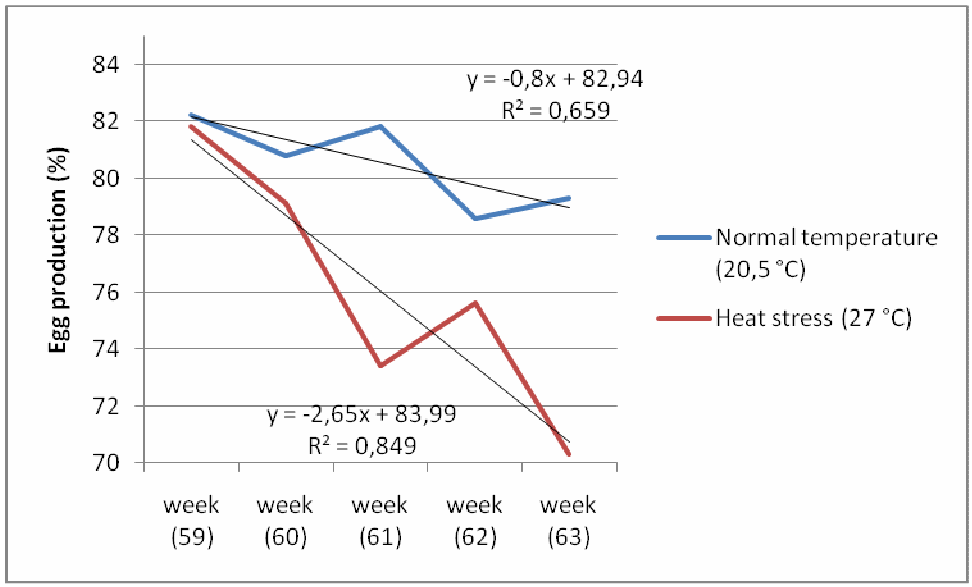

Fig. 2. Production parameters of laying hens as affected by heat stress

Parameters of acid-base balance are presented in Table 2. Acid-base parameters of laying hens were affected by heat stress. Highly significant differences were found for the parameters pCO_2 and $st.HCO_3$. Blood pH values were not altered in the first 2 weeks of heat stress exposure. Changed values of pCO_2 and $st.HCO_3$ can be regarded as the state compensated respiratory alkalosis. Although, the next period the heat stress expected alkalosis, the effect was not confirmed.

Table 2

Parameters of acid-base balance

	week	60		61		62		63	
		Mean	**SE**	**Mean**	**SE**	**Mean**	**SE**	**Mean**	**SE**
pH	20.5°C	7.371	0.0032	7.372	0.0015	7.383	0.0021	7.378	0.0014
	27°C	7.372	0.0029	7.371	0.0011	7.380	0.0018	7.289	0.0008
pCO_2	20.5°C	37.23	0.081	36.84	0.095	37.12	0.084	37.20	0.094
	27°C	27.53	0.064	25.18	0.097	26.72	0.077	25.91	0.068
$st.HCO_3$	20.5°C	27.21	0.042	27.43	0.122	27.61	0.075	26.83	0.066
	27°C	22.41	0.033	21.83	0.093	22.01	0.052	25.76	0.071
BE	20.5°C	0.35	0.775	3.28	0.680	2.16	0.543	–2.81	0.449
	27°C	–3.83	0.341	–4.31	0.337	–6.25	0.447	–1.16	0.326

Conclusion

Heat loss in poultry is limited due to feathering and the absence of sweat glands. When the temperature and relative humidity exceed the comfort level, it loses the ability to efficiency dissipate heat. Biochemical parameters of internal environment of hens are suitable indicator to evaluate comfort level of animals. Therefore, our study was focused on the effect of heat stress on biochemical parameters of hens.

Acid-base parameters of laying hens were affected by heat stress. Significant differences were found in pCO_2 and $st.HCO_3$. Blood pH values were not altered in the first 2 weeks of heat stress exposure. Changed values of pCO_2 and $st.HCO_3$ can be regarded as the state compensated respiratory alkalosis.

To confirm these data, there is necessary next exploration to reveal detail effects of heat stress on biochemical and production parameters of laying hens.

Acknowledgments

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Anna KWIECIŃSKA[1] and Krystyna KONIECZNY[1]

RECOVERY OF INDUSTRIAL WATER FROM PIG SLURRY BY MEANS OF MEMBRANE TECHNIQUES

ODZYSK WODY PRZEMYSŁOWEJ Z GNOJOWICY TRZODY CHLEWNEJ Z WYKORZYSTANIEM TECHNIK MEMBRANOWYCH

Abstract: Slurry that is produced during high density livestock farming requires proper utilization methods. Nowadays, it is mainly used as a fertilizer or as a substrate for biogas or compost production. However, these methods are often very limited and do not allow to utilize the total amount of produced slurry, thus it is still treated as a problematic waste. High water content in slurry leads to the assumption that it can be treated as a water source. This assumption is quite realistic if application of low and high pressure membrane techniques is considered. Such a solution would allow not only to recover water that could be further reused on farms, but also to obtain valuable concentrated nutrients solution which can be used as a fertilizer and easily transported to agricultural areas. The aim of the study was to determine the effectiveness of water recovery from pig slurry using integrated system: centrifugation/two step ultrafiltration/nanofiltration. The first step ultrafiltration was performed using PVDF membrane of cut off 100 kDa while the second step using PES membrane of cut off 10 kDa. During the polishing process i.e. nanofiltration, hydrophilic composite membrane of cut off 200 Da was used. The effectiveness of the process was determined basing on the change of values of such parameters like: BOD_5, COD, contents of TOC, IC, TC, N_{tot}, concentrations of NH_4^+, Cl^-, SO_4^{2-}, PO_4^{3-}, Mg^{2+}, Ca^{2+}, K^+, while the capacity of the treatment was determined using volumetric permeate streams. Obtained results allow to conclude that the proposed system can be used to recover water of an industrial quality.

Keywords: manure, water recovery, membrane processes, ultrafiltration, nanofiltration

High density livestock farming results in the production of a significant amount of slurry which is a mixture of animal urea, feces and water [1]. Nowadays, it is mainly used as a fertilizer or a substrate for biogas or compost production. In Poland, 70 mln m^3 of slurry is produced every year, however only ca 21 mln m^3 is applied for fertilizing purposes [2], whereas the rest is treated as a highly load waste and requires special treatment methods. However, except from nutrient substances, slurry contains also a significant amount of water (ca 90÷97%) which is usually omitted product during consideration of slurry management methods.

The development and improvement of membrane processes create the possibility of water recovery from slurry [3, 4]. The application of low and high pressure membrane techniques would allow to obtain proper quality of water that could be reused on farms. The recovery of water would be a great advantage in areas which deal with its deficit and the concentrated fertilizing mixtures could be easily transported to agriculture areas.

Materials and methods

50 dm^3 sample of a pig slurry was collected from a 13.000 m^3 lagoon localized at one of the high density livestock farm in Silesia region. Firstly, the slurry was centrifuged for 10 minutes with the rotational speed of 15.000 rpm. The obtained supernatant was then

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introduced to the laboratory membrane cell by Koch (Fig. 1). The device is equipped with the 0.5 dm^3 feed tank and the effective separation area of the installed flat membrane is equal to 28 cm^2. All processes were carried out in the cross flow mode.

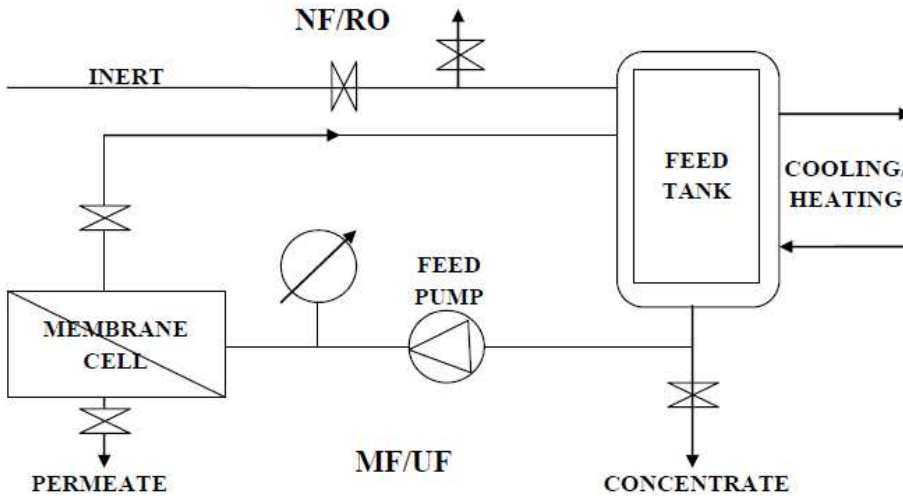

Fig. 1. The scheme of the laboratory installation for membrane filtration by Koch

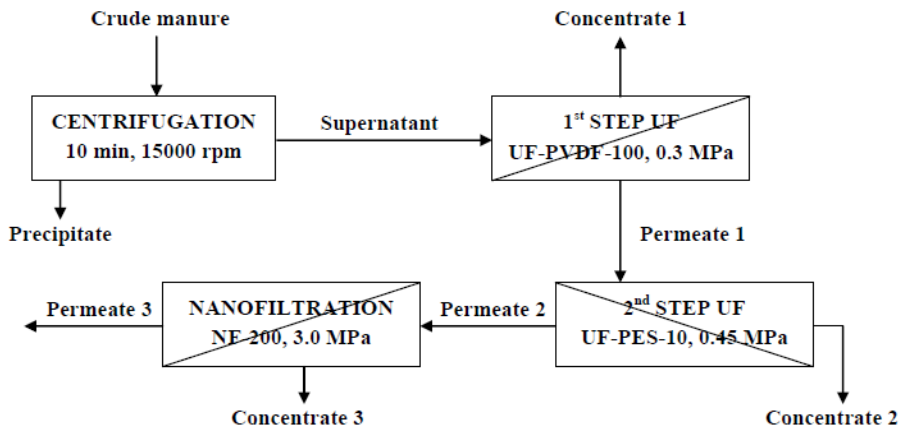

Fig. 2. The scheme of the pig slurry treatment process in the integrated system of centrifugation/two step ultrafiltration/nanofiltration

Firstly, 100 kDa polyvinylidene fluoride (UF-PVDF-100) membrane was used for ultrafiltration of the supernatant and the permeate was introduced to the second ultrafiltration step. The second process was carried out with the use of 10 kDa polyethersulfone (UF-PES-10) membrane. The polishing process applied for the treatment of the second ultrafiltration step permeate was performed using composite nanofiltration

membrane of cut off 200 Da (NF-200). All applied membranes were provided by KOCH. The detailed scheme of the process is shown in Figure 2.

Following parameters were analyzed in the produced process streams: pH, conductivity, COD, BOD_5, contents of TOC, IC, TC, N_{tot}, concentrations of ions NH_4^+, PO_4^{3-}, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, (Na^+ - only in nanofiltration permeate). COD, concentrations of K^+, PO_4^{3-}, $N_{tot.}$ and NH_4^+ were determined according to Merck methodology, while BOD_5 by means of the respirometric method with the use of the OXI Top WTW set. Concentrations of Cl^- and SO_4^{2-} ions were obtained during chromatographic analysis using ionic chromatograph DX 120 by Dionex. The content of particular carbon forms was analyzed using Multi N/C analyzer by Jena Analytic. Concentrations of Ca^{2+} and Mg^{2+} were determined by means of the classical titration method while Na^+ content using flame photometer.

The slurry membrane filtration was preceded by the determination of the volumetric deionized water stream under process pressure for all membranes applied. When particular slurry treatment processes were finished membranes were washed with deionized water and the volumetric stream was also measured.

Results and discussion

The obtained results indicated that the proposed system of integrated centrifugation/two step ultrafiltration/nanofiltration was sufficient for the slurry treatment. The improvement of the quality of treated streams was observed in every step (Table 1). However, finally obtained permeate did not fulfill the regulations for the drinking water quality [5] according to the concentrations of TOC and NH_4^+ ion, which were exceeded, and to the absence of Mg^{2+} and Ca^{2+} ions.

Table 1

The comparison of parameters of treated streams

Parameter	Unit	Crude slurry	Supernatant	Permeate 1	Permeate 2	Permeate 3 (water)
pH	-	7.36	7.69	8.1	8.17	8.6
Conductivity	[mS/cm]	5.96	5.84	5.75	5.6	0.675
TOC	[mg/dm^3]	1134	671	528	381	9.7
IC	[mg/dm^3]	466	437	420	370	44
TC	[mg/dm^3]	1600	1108	948	751	53.7
COD	[mg O_2/dm^3]	7560	3785	2990	2285	13.9
BOD_5	[mg O_2/dm^3]	3000	2900	1500	480	n/m*
NH_4^+	[mg/dm^3]	1350	1200	1478	1414	135
N_{tot}	[mg/dm^3]	3100	2950	2950	2950	148
SO_4^{2-}	[mg/dm^3]	199	192	185	49.8	0
PO_4^{3-}	[mg/dm^3]	63.1	34.6	32.2	24.7	0
Cl^-	[mg/dm^3]	385	373	371	311	52
K^+	[mg/dm^3]	820	805	790	790	180
Mg^{2+}	[mg/dm^3]	19.2	16.8	14	11	0
Ca^{2+}	[mg/dm^3]	100	100	88	80	0
Na^+	[mg/dm^3]	-	-	-	-	41.2

*non-measurable

The measurements of volumetric streams indicated that the fouling of all applied membranes occurred during the slurry filtration (Fig. 3). Both types of fouling were observed, reversible and irreversible, however the second fouling type occurred only in case of ultrafiltration membranes and was mostly noticeable during the first step UF process. The applied washing of membranes with distilled water allowed to partially recover the initial capacity for UF membranes, while in case of the NF membrane the post-process stream was even greater than the initial one. That can be explained by the modification of the membrane surface, which could have been caused by calcium and magnesium ions present in the manure as well as by organic substances.

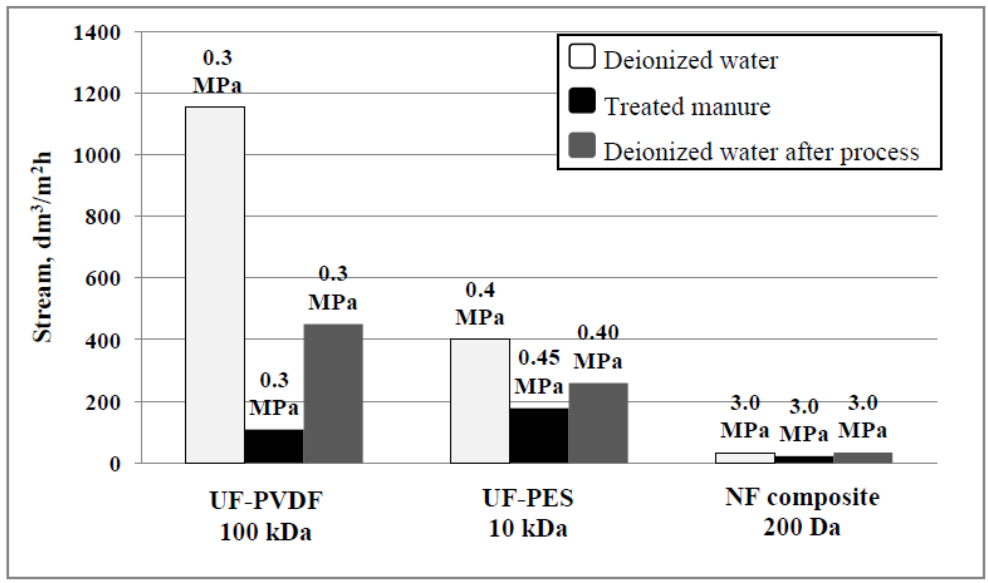

Fig. 3. The comparison of volumetric streams of the deionized water (before and after the process) and the treated slurry determined for all membranes

Conclusions

The presented study focused on the recovery of the industrial water from the pig slurry by means of the integrated system comprised of centrifugation/two step ultrafiltration /nanofiltration.

Obtained results allowed to conclude that the proposed system is suitable for that purpose and the final permeate could be reused on farm eg for animals or farmahouses washing. However, the obtained water did not fullfill the regulations for drinking water quality as concentrations of ammonium ion and TOC were exceeded and it did not contain magnesium and calcium ions.

The appearance of fouling phenomenon was observed in case of all membranes, however, it greatest influence on the membrane capacity was observed in case of UF membranes. Additionally, for these membranes both form of fouling, reversible and irreversible, were present. The washing of membranes with distilled water did not allow to

recover the initial capacity for UF membranes, while for NF membranes the post-process water stream was greater than the initial one. That was explained by the possible modification of membrane surface, probably by magnesium and calcium ions as well as the organic substances.

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ODZYSK WODY PRZEMYSŁOWEJ Z GNOJOWICY TRZODY CHLEWNEJ Z WYKORZYSTANIEM TECHNIK MEMBRANOWYCH

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Abstrakt: Gnojowica powstająca podczas wielkoprzemysłowej hodowli zwierząt wymaga stosowania odpowiednich metod utylizacji. Obecnie jest ona wykorzystywana jako nawóz bądź też substrat do produkcji biogazu oraz kompostu. Jednakże metody te są często ograniczone i nie pozwalają na zagospodarowanie całkowitej ilości powstającej gnojowicy, stąd też wciąż jest ona traktowana jako uciążliwy odpad. Wysoka zawartość wody w gnojowicy pozwala założyć, iż może być ona traktowana jako źródło wody. To założenie jest całkiem realne w przypadku zastosowania nisko- i wysokociśnieniowych procesów membranowych. Takie rozwiązanie pozwoliłoby nie tylko na odzysk wody, która mogłaby zostać ponownie wykorzystana na farmie, ale także na otrzymanie wartościowych, stężonych roztworów substancji odżywczych, które mogłyby zostać wykorzystane jako nawóz i łatwo transportowane na tereny rolnicze. Celem przeprowadzonych badań było określenie efektywności odzysku wody z gnojowicy trzody chlewnej, wykorzystując zintegrowany system: wirowanie/dwustopniowa ultrafiltracja/nanofiltracja. Pierwszy stopień ultrafiltracji prowadzono z użyciem membrany z PVDF o cut off 100 kDa, drugi zaś stopień z wykorzystaniem membrany z PES o cut off 10 kDa. Podczas etapu doczyszczania, tj. nanofiltracji, zastosowano kompozytową membranę hydrofilową o cut off 200 Da. Efektywność procesu określono, bazując na zmianie wartości parametrów, jak: BZT_5, ChZT, zawartości OWO, WN, OW, $N_{cał}$, stężenia jonów NH_4^+, Cl^-, SO_4^{2-}, PO_4^{3-}, Mg^{2+}, Ca^{2+}, K^+, wydajność zaś wyznaczono na podstawie objętościowych strumieni permeatów. Przeprowadzane badania pokazują, że zaproponowany system może zostać wykorzystany do odzysku wody o jakości przemysłowej.

Słowa kluczowe: gnojowica, odzysk wody, procesy membranowe, ultrafiltracja, nanofiltracja

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POSSIBILITIES OF ALTERNATIVE FUEL (BIOFUEL) APPLICATION IN INDUSTRY

MOŻLIWOŚCI ZASTOSOWANIA PALIW ZASTĘPCZYCH (BIOPALIW) W PRZEMYŚLE

Abstract: Apart from the growing requirements related to environmental protection and imposed emission limits, the industry is encountering yet other difficulties. It regards, eg the increasing prices of fossil fuels, which are the key factor determining the production costs and the final price of the product. In these circumstances it appears to be reasonable to use alternative fuels, which could facilitate the achievement of lower level of harmful substances emission without lowering the quality of the obtained final product and reduce production costs. Moreover, the application of the fuels alternative to the typical fossil fuels used in industry could protect it from a probable situation where natural resources of the currently used fuels run out or their accessibility is hampered. In a technical process, fuel should comply with specific technical and economic requirements as well as possess necessary physicochemical properties. We also need to consider a number of factors which may limit the application of specific fuels due to the equipment operation conditions (eg furnaces), the permissible final plant emission and the required quality of the final product. These are mainly its fuel and physicochemical properties that determine the application of particular fuel.In the article laboratory test results of four possible alternative fuels (biofuels) and mazout treated as a reference substance are discussed and the compliance of each fuel with established requirements is specified.

Keywords: alternative fuels, biofuels, industry, mazout, fuel properties

Fuel applied in technical processes should comply with specific technical and economic requirements as well as possess necessary physicochemical properties. Moreover, there is a number of factors limiting the possibility of fuel applications which are the result of the furnace operation conditions, permissible final plant emission and required quality of the final product. Usage of alternative fuel should be economically justified - the costs of obtaining fuel resources should be reasonable and their producer (supplier) should ensure the continuity of supply. Applied fuel should, above all, meet the requirements of the plant where it is to be used. The behaviour of a specific substance in the process conditions should be known and it should be adjusted to those conditions [1]. These are mainly its fuel and physicochemical properties that determine the application of a particular fuel.

Alternative fuels under study

Laboratory tests were intended to determine the fuel and physicochemical properties of liquid fuels considered for the application in industry.

Five types of liquid fuels were used for tests:

- mazout,
- two types of petrol produced based on plastics - KTSF,
- technical glycerol,
- animal fat - Saria.

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Mazout

Mazout is currently one of the basic liquid fuels used in industry. Its calorific and emission properties as well as its behaviour in the process conditions are known. In the conducted tests, mazout was treated as a reference substance.

Petrols produced based on plastics - KTSF

KTSF is a substance produced based on plastics. Raw materials used for its production include mainly polyolefines, that is polyethylene (PE) and polypropylene (PP) derived from wastes, usually packaging. The final product is applicable in petrochemistry for fuel production, household chemistry as raw material for the manufacturing of such chemical products as eg: paraffins, pastes, lubricants and dividing liquids [2].

Two KTSF samples were used for testing. The first sample contains 20% of the final product, the second sample contains 80% of the final product.

Technical glycerol

Glycerol is formed in the process of esterification of plant oils which results in the formation of methyl esters of higher fatty acids (biodiesel). Plant oils most commonly used for the process of glycerol production include: colza, sunflower, soybean, maize as well as palm and olive oils [3].

Technical glycerol is used as a substance for chemical syntheses and as a semi-finished product for the production of pharmaceutical glycerol in the process of low pressure distillation. Technical glycerol is not classified as a hazardous substance, it is biodegradable and does not pose a threat to human health. It is an inflammable substance, its vapours are heavier than air and it may form flammable mixtures with air [4].

The yearly growing processing capabilities of plants for biodiesel production result in the overproduction of glycerol in Europe to the extent which exceeds the demand of the cosmetic and pharmaceutical industry. Therefore, a gradual decrease of the price of this substance is predicted as well as the intensification of researches on the economic application of technical glycerol [5].

Animal fat - Saria

Saria is a fuel produced based on animal wastes derived from agriculture and food industry (slaughter houses, plants processing animal products). This substance is produced inter alia as the result of processing of the fat derived from dead animals or those slaughtered not for consumption purposes as well as from animal wastes derived from animals intended for consumption, including fish wastes [1].

Fuel and physicochemical properties testing

Fuel and physicochemical properties testing covered the evaluation of the content of:

- sulphur,
- carbon,
- hydrogen,
- measurement of the ignition temperature,

- chlorides,
- combustible particles,
- determination of gross calorific value,
- calculation of calorific value.

Laboratory tests were conducted in the laboratory of the Department of Technologies and Installations for Waste Management, pursuant to the applicable methods and standards.

Analysis of the obtained results and alternative fuel selection

As regards the calorific value of tested fuels, KTSF petrols based on plastics showed most advantageous results. They have the highest calorific value (44 151 kJ/kg and 44 963 kJ/kg), greater than mazout (42 150 kJ/kg) and Saria (37 317 kJ/kg). Technical glycerol had the least advantageous results, since its calorific value amounted merely to 16 450 kJ/kg.

Carbon and hydrogen content reached similar levels in all fuels (77.44÷88.78% carbon and 9.42%÷11.09% hydrogen), only in case of glycerol the content of these elements was significantly lower (35.03% carbon and 5.09% hydrogen). Sulphur content was highest in mazout (1.48%). In other fuels it did not exceed 0.5% and for KTSF petrol of the 2nd sample it amounted to 0%.

In case of aggressive compounds which include chlorides, all tested fuels demonstrated their content within the following range: from 305.4 mg/kg (mazout) to 601.5 mg/kg (KTSF petrol of 2nd sample) calculated to HCl. All tested fuels have high content of combustible matter - in all cases it amounted to over 99%.

The ignition temperature value, depending on the type of fuel, reached various levels. For KTSF petrol, the ignition occurred already at 26 and 27ºC. The ignition temperature of mazout was 86ºC. The highest ignition temperature was discovered in case of Saria (244ºC) and technical glycerol (256ºC).

Summary and conclusions

Based on the analysis of the conducted tests, technical glycerol and KTSF petrols were excluded from the considerations about using them as alternative fuels. Technical glycerol was rejected due to its too low calorific value, while KTFS petrols were eliminated due to the very low ignition temperature, which poses a threat to the process safety. It was concluded that only animal fat, Saria, may be qualified for the application in a thermal process.

Conduction of a combustion process with the usage of alternative fuel without co-combustion with mazout would be difficult to perform both due to technological reasons (Saria's parameters are less stable than those of mazout and its properties may differ depending on the supply) and due to the strict emission standards for fuels produced from wastes. Therefore, it is suggested to co-combust Saria with mazout in the proportion of 40% of Saria to 60% of mazout.

However, the application of additional fuel in the form of Saria is connected with expenses for the assembly of a required continuous monitoring system of gas impurities in the plant as well as with other difficulties resulting from the environmental regulations. Namely, the plant where co-combusted fuels are produced from waste animal fats must

comply with the regulations on waste co-combustion plant, and consequently, with much more strict emission standards for specific substances emitted from the plant.

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MOŻLIWOŚCI ZASTOSOWANIA PALIW ZASTĘPCZYCH (BIOPALIW) W PRZEMYŚLE

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Abstrakt: Poza zwiększającymi się wymogami związanymi z ochroną środowiska oraz nakładanymi limitami emisyjnymi przemysł napotyka na coraz to inne utrudnienia. Dotyczy to m.in. wzrastających cenach paliw kopalnych, które są kluczowym czynnikiem determinującym koszty produkcji oraz cenę końcową produktu. W tej sytuacji uzasadnione wydaje się być zastosowanie paliw zastępczych, dzięki którym można by osiągnąć niższy poziom emisji substancji szkodliwych bez obniżenia jakości otrzymywanego produktu końcowego oraz obniżyć koszty produkcji. Ponadto stosowanie w przemyśle paliw alternatywnych dla typowych paliw kopalnych mogłoby chronić go przed trudnościami spowodowanymi wyczerpywaniem się zasobów naturalnych używanych obecnie paliw lub też dostęp do nich stałby się utrudniony. W procesie technicznym paliwo powinno spełniać określone wymogi techniczne, ekonomiczne oraz mieć odpowiednie właściwości fizykochemiczne. Należy również mieć na uwadze szereg czynników, które mogą ograniczyć zastosowanie określonych paliw ze względu na warunki eksploatacyjne urządzeń (np. pieców), dopuszczalną emisję końcową z instalacji oraz wymaganą jakość produktu końcowego. O zastosowaniu danego paliwa decydują głównie jego właściwości paliwowe i fizykochemiczne. W artykule omówiono wyniki badań laboratoryjnych czterech potencjalnych paliw zastępczych (biopaliw) oraz mazutu, traktowanego jako substancja odniesienia, a także określono zgodność każdego z paliw z wyznaczonymi wymaganiami.

Słowa kluczowe: paliwa zastępcze, biopaliwa, przemysł, mazut, właściwości paliwowe

Joanna MATUSKA-ŁYŻWA[1]

ASSESSMENT OF THE INVASIVENESS OF ENTOMOPATHOGENIC NEMATODES *Heterorhabditis megidis* FROM SELECTED GRASSLANDS

OCENA INWAZYJNOŚCI NICIENI ENTOMOPATOGENNYCH *Heterorhabditis megidis* POCHODZĄCYCH Z WYBRANYCH UŻYTKÓW ZIELONYCH

Abstract: The use of entomopathogenic nematodes as biological means of plant pest control focussed the attention on relationships between soil contamination with heavy metals and survival of nematodes in the soil habitat. Negative properties of heavy metals (including lead) disturb life functions of entomopathogenic nematodes. The effect of low habitat contamination with lead on the development of subsequent generations of entomopathogenic nematodes *Heterorhabditis megidis* was studied in performed experiments. Study area was situated near Torun, Opole, and Skarzysko-Kamienna. Grain size structure, total lead content and pH were analysed in soil samples. Nematodes from own laboratory culture were used as a control. Nematodes isolated from soil samples with the method of Bedding and Akhurst were determined to species as *H. megidis*. Larvae that left the host's (*Galleria mellonella* L.) body were used to infect the next test insects in the laboratory. Six passages were performed in total. Extensity and intensity of infection by *H. megidis* were determined in subsequent passages.

Keywords: entomopathogenic nematodes, *Heterorhabditis megidis*, *Galleria mellonella*, heavy metals, lead ions

The activity of soil entomopathogenic nematodes depends on many environmental factors. Soil structure, soil temperature and moisture affect nematode biology [1].

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

Another equally important factor influencing nematode activity is soil pH. Natural acidification associated with the presence of carbon dioxide in the air prevails in the soils of Poland. This gas when dissolved in rain waters forms weak carbonic acid which falls to the soil with atmospheric precipitation. In agricultural lands soil pH varies between 4.0 and 7.2. The pH value above 8.3 might indicate the presence of antropogenically derived alkalizing substances like eg metal oxides. Optimum pH for biological processes associated with the metabolism of plants and soil organisms is considered to be in range from 5.5. to 7.2 [3]. The mobility, activity and pathogenic properties of entomopathogenic nematodes are higher at pH 6.8 and 8 than at pH 5.5 [4].

Soil pH largely decides upon the bioavailability and mobility of heavy metals. Both features increase with soil acidification [3]. Heavy metals, particularly lead, unfavourably affect nematode invasiveness and reproduction [5-8].

Local populations of nematodes are well fit to changing habitat conditions and may efficiently control insect populations dwelling the same habitat [9].

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Studies carried out on the entomopathogenic nematode-host insect system indicate that multiple infection of insects of a given species results in selection of a specific nematode race which is more pathogenic than the initial race [10, 11]. This may suggest that local populations of entomopathogenic nematodes differentiate under the effect of a characteristic species composition and domination structure of local insect communities [12].

The aim of performed studies was to analyse the invasiveness in subsequent passages through the same insect species of entomopathogenic nematodes *Heterorhabditis megidis* (Poinar, Jackson and Klein 1987) originating from natural habitats and to analyse acidification, grain size structure and lead content in these habitats.

Material and methods

Studies were carried out in the summer seasons of the years 2008-2009. Fifty soil samples were taken with the Egner's sampler from a soil layer 0÷25 cm in three selected study areas (natural meadows). Physical and chemical soil properties were analysed in the Analytical Centre and the Department of Soil Science of the Warsaw University of Life Sciences (SGGW). Grain size structure, total lead content with the flame AAS method and soil pH with the potentiometric method (acc. to the pB procedure, 2nd ed. of 21.06.2005) were determined. Nematodes isolated from soil samples with the method of Bedding and Akhurst [13] were identified as *Heterorhabditis megidis* using keys for species determination.

Experiment was carried out in the Sanyo MIR 253 incubator at 25ºC. Nematode larvae isolated from soil samples were used to infect test insects (*Galleria mellonella* of a mean body weight of 0.160 g) using the invasive dose of 50 nematode larvae per insect on Petri dish. Half of insects dead as a result of nematode infection were dissected to determine the intensity of invasion and the second half were transferred to White's trap [14] to obtain invasive larvae migrating from the host's body. The larvae leaving the host's body were used to infect next test insects (*G. mellonella* L.). Six subsequent passages were made in total. Insects' mortality and the extensity and intensity of invasion of *H. megidis* were determined in every passage. Nematodes bred in the laboratory for years in one host (*G. mellonella*) were used as control in the assessment of subsequent passages. The experiment was repeated twice.

Results and discussion

Physical and chemical properties of analysed soil samples were appropriate for nematode larvae living in soil habitat. Soil samples had natural lead content (from 5.894 to 16.93 mg/kg) and pH from moderately to weakly acidic. Grain size structure of analysed soil samples was typical for loamy sand and weak loamy sand. The highest survival of nematodes was noted in such habitats [2] (Tab. 1).

Table 1

Characteristics of studied sites

Location	Longitude	Latitude	Grain size structure	pH	Pb [mg/kg]
Skarzysko-Kamienna	20,54,49 E	51,07,10 N	Loamy sand	5.4	9.50
Torun	18,20,15 E	53,03,03 N	Weak loamy sand	5.34	5.894
Opole	17,45,45 E	50,41,17 N	Loamy sand	6.07	16.93

Differences in the invasiveness of nematodes isolated from studied soil habitats were observed in subsequent passages. Initially, the invasion of nematodes was slow (insects' death after 72 hours) and lower than in the control sample. Insect mortality, extensity and intensity of invasion were low at that period. In subsequent passages faster killing of test insects was observed (insects' death after 48 hours) and the increase of invasiveness manifesting itself by high insect mortality and the extensity and intensity of invasion. After several passages the invasiveness of nematodes from the field was the same as that of nematodes bred in the laboratory for many years without changing their host (Figs 1-3).

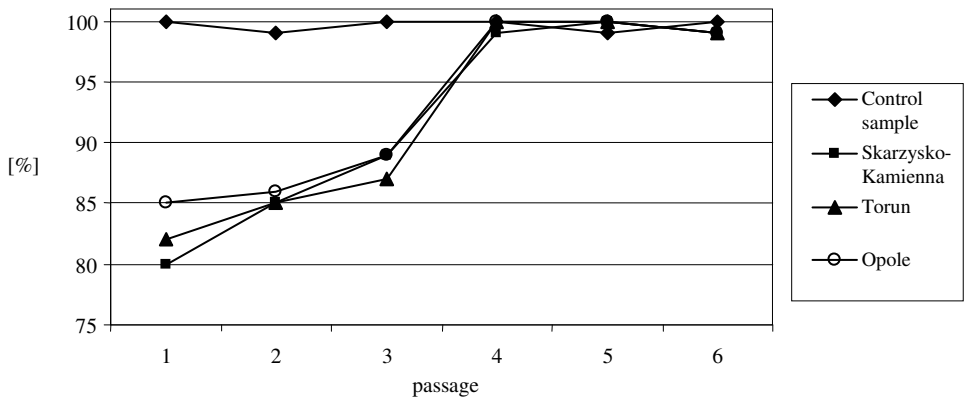

Fig. 1. Mortality [%] of test insects in subsequent passages

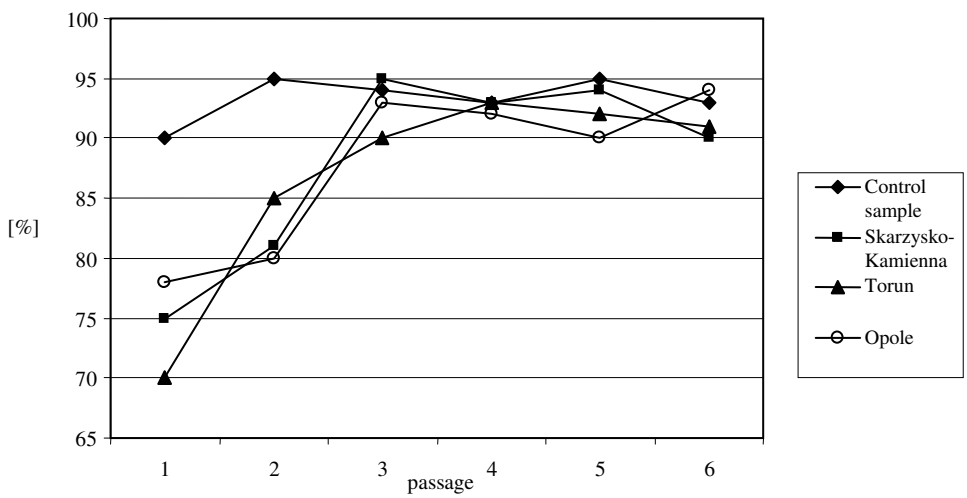

Fig. 2. Extensity [%] of invasion of *H. megidis* in subsequent passages

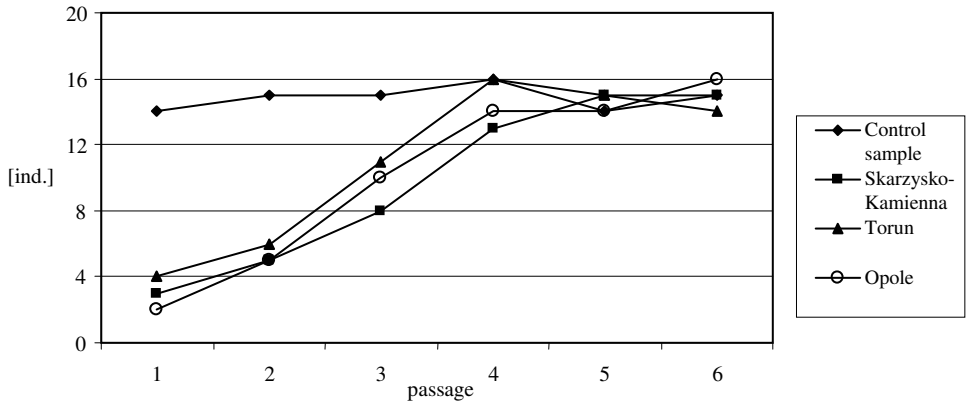

Fig. 3. Intensity [ind.] of invasion of *H. megidis* in subsequent passages

Performed statistical analysis (ANOVA) for the intensity of invasion showed highly significant differences between the control sample and all studied groups of nematodes in passages 1-4. Significant differences were also found in the intensity of invasion in the 3rd and 4th passage between nematodes from all analysed habitats.

A lack of significant differences between the control nematodes and those from natural sites in the 5th and 6th passage may indicate that multiple infections of insects from a given species may lead to selection of such a nematode race which is more pathogenic for this host species than nematodes from the initial race. Results of this study confirm the findings of other authors [10, 11, 15].

Conclusions

Performed studies allow for concluding that multiple passage of entomopathogenic nematodes through the host's organism of a single species increased nematodes' pathogenicity in comparison with initial population. Hence, nematode populations may vary under the effect of species composition and domination structure of local communities of host insects.

Acknowledgements

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OCENA INWAZYJNOŚCI NICIENI ENTOMOPATOGENNYCH *Heterorhabditis megidis* POCHODZĄCYCH Z WYBRANYCH UŻYTKÓW ZIELONYCH

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Abstrakt: Wykorzystanie nicieni entomopatogennych jako biologicznego środka zwalczającego szkodniki roślin spowodowało zwrócenie uwagi na zależności między skażeniem gleb metalami ciężkimi a przeżywalnością larw nicieni w środowisku glebowym. Szkodliwe właściwości metali ciężkich, w tym ołowiu, zaburzają funkcje życiowe nicieni owadobójczych. W przeprowadzonych doświadczeniach zbadano wpływ niskiego skażenia środowiska ołowiem na rozwój kolejnych pokoleń nicieni entomopatogennych *Heterorhabditis megidis*. Tereny badawcze znajdowały się w okolicach miejscowości: Toruń, Opole, Skarżysko-Kamienna. W próbkach glebowych oznaczono skład granulometryczny, całkowitą zawartość ołowiu w glebie oraz odczyn gleby. Kontrolę stanowiły nicienie pochodzące z laboratoryjnej hodowli własnej. Wyizolowane z próbek glebowych metodą Beddinga i Akhursta (1975) nicienie oznaczono na podstawie kluczy do oznaczania gatunku jako *H. megidis*. Larwami, które opuściły ciało żywiciela (*Galleria mellonella* L.), zarażono laboratoryjnie kolejne owady testowe. Wykonano 6 pasaży. Oznaczono ekstensywność i intensywność inwazji *H. megidis* w kolejnych pasażach.

Słowa kluczowe: nicienie entomopatogenne, *Heterorhabditis megidis*, *Galleria mellonella*, metale ciężkie, jony ołowiu

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COMPARISON OF POLYAMINE CONTENT IN LEAVES OF BARLEY PLANTS GROWN IN NICKEL STRESS CONDITIONS, CAUSED BY INORGANIC AND CHELATIC NICKEL

PORÓWNANIE ZAWARTOŚCI POLIAMIN W LIŚCIACH JĘCZMIENIA UPRAWIANEGO W WARUNKACH STRESU POWODOWANEGO PRZEZ NIKIEL W FORMIE NIEORGANICZNEJ I CHELATOWEJ

Abstract: In a pot experiment the effect of inorganic and chelatic nickel on the metabolism of polyamines in leaves of spring barley plants cv. Poldek was examined. Nickel was applied to acid soil in the form of $NiSO_4 \cdot 7H_2O$ and Ni-EDTA (M:L 1:1) in the doses of 50 and 75 mg Ni · kg^{-1} of soil. After a 10-day exposition of plants to the effect of inorganic and chelatic nickel, the content of putrescine in leaves increased, whereas the content of spermine and spermidine decreased. In stress conditions caused by inorganic nickel the increase of putrescine content and the decrease of spermine and spermidine content in barley leaves were much bigger than in stress conditions caused by chelatic nickel.

Keywords: nickel stress, spermidine, spermine, spring barley, putrescine

In stress conditions caused by different factors metabolism of polyamines in plants changes and the intensity and direction of these changes depend on the genotype of the plant as well as on the type, concentration and duration of the effect of the stress factor [1-3]. Results of studies conducted so far have shown that metabolism of polyamines changes also in response to nickel stress [4-6]. Specificity of these changes lies in the fact that accumulation of putrescine in plant tissues increases, whereas the content of spermine and spermidine decreases. In spite of the fact that putrescine takes part in inactivating free radicals generated in plant cells in stress conditions [5], putrescine is believed to be a hormone which speeds up the ageing of plants [7, 8]. On the other hand, spermine and spermidine delay the process of plant ageing and their main function in stress conditions consists in protecting cell membranes from damage [9-12].

The research on the metabolism of polyamines in plants in response to nickel stress conditions conducted so far have concentrated on the stress caused by inorganic form of this metal. However, nickel, as a *d*-electrone metal, easily forms chelate compounds with low-molecular-weight organic compounds in the environment [13-16]. It is in the form of chelates that this metal appears in the environment as a pollutant, ie as a component of sewage and industrial waste and of waste sludge [14-16]. Consequently, it is accessible to plants in large amounts in the form of complex ions. The main purpose of this study was to find out the direction of changes of metabolism of polyamines in the leaves of spring barley cv. Poldek exposed to nickel stress conditions caused by inorganic and cheltic forms of this metal.

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Materials and methods

Spring barley plants cv. Poldek were grown in pot cultures on average-quality soil, whose granulometric composition was that of silt. The soil had the following properties: float particles - 28%, organic C - 0.8 mg · kg^{-1}, sorption capacity - 11.8 cmol(+)kg^{-1}, pH 5.2, total Ni content - 11.8 mg · kg^{-1}, content of Ni soluble forms in 1 mol · dm^{-3} HCl - 2.4 mg · kg^{-1}. Basic fertilization was applied in the experiment; fertilization amounts per pot were the following: 1 g of N in the form of NH_4NO_3, 0.5 g of P - $Ca(H_2PO_4)_2$, 0.8 of K - KCl and 0.3 mg of Mg in the form of $MgSO_4$. Plant vegetation was conducted in growth chamber at 20ºC and at relative humidity of 75%, for a long (16-hour) photoperiod with light intensity of 180 µmol · m^{-2} · s^{-1}. Nickel was added to the soil at the stage of plant germination in the form of $NiSO_4 \cdot 7H_2O$ and Ni-EDTA (M:L 1:1) in the doses of 50 and 75 mg Ni · kg^{-1}.

Samples of leaves were harvested after 10 days of plant growth in the conditions of excess of nickel for the analysis of polyamine content. The content of polyamines (PAs) was determined by means of the spectrofluorometric method described by Kaur-Sawhney et al [17]. Extraction of PAs was conducted in 5% $HClO_4$. Dansylation of PAs was conducted by means of dansyl chloride (5 mg/cm^3 acetone) and 200 mm^3 of saturated solution of Na_2CO_3. The dansylated PAs were extracted in 0.5 cm^3 of toluene and after a careful separation the organic fraction was collected on plates covered with silica gel G, in system chloroform: triethylamine (25:2 v/v). Derivatives of the particular polyamines were located by comparing them with appropriate standards in UV light. After TLC, the dansylopolyamine bands were scraped, the residue is eluted in 2 cm^3 of ethylacetate; then the acetate was evaporated and dry samples were dissolved in 5 cm^3 of methanol. Quantitative determination of dansyl derivatives of PAs was made by means of the spectrofluorometric method, at an excitation band λ = 336 nm, and an emission band λ = 515 nm.

Statistical analysis: Variance analysis (ANOVA) of obtained data was carried out, followed by a test checking the significant difference (LSD) with probability of 0.05.

Results and discussion

Nickel used in fertilization of spring barley (*Hordeum vulgare* L.) cv. Poldek influenced on metabolism of polyamines in leaf tissues (Fig. 1). In general, after a 10-day exposure of spring barley to the effect of inorganic and chelatic nickel, the content of polyamines in leaves decreased in the case of both chemical forms; however, the decrease was small (Fig. 1). When the soil was contaminated with inorganic nickel added in the amount of 50 and 75 mg · kg^{-1}, the content of all the three polyamines (Putrescine+Spermine+Spermidine) was smaller by about 4.1% and 4.6% as compared with the control. When the soil was contaminated with Ni-EDTA added in the amount of 50 and 75 mg · kg^{-1}, the content of these polyamines was lower than in the control by 0.5% and 4.1%, respectively. The direction of changes in metabolism of polyamines in barley leaves was specific to this metal and did not depend on its chemical form; the content of putrescine increased and the content of spermine and spermidine decreased (Fig. 1). However, the intensity of metabolism of polyamines depended on the doses and chemical form of nickel applied to the soil; it should be noted that it depended on its chemical form to a greater extent (Fig. 1). After 10 day's growth on soil contaminated with nickel sulphate

added in the amount of 50 and 75 mg · kg^{-1}, the content of putrescine in barley leaves increased by 64.4 and 80.6%, respectively, as compared with the content of this polyamine in control barley leaves (Fig. 1). After the same time of growth of plants in the presence of Ni-EDTA chelate which was applied to the soil in the amount of 50 mg Ni · kg^{-1}, the content of putrescine in the leaves increased only by 11.5% (Fig. 1). A significant increase in the content of this polyamine (by 32.2% as compared with the control) was observed when the soil was contaminated with a larger amount of nickel chelate, ie 75 mg Ni · kg^{-1} of the soil; however, also in this case the increase in the content of putrescine was smaller than when the soil was contaminated with inorganic nickel (Fig. 1).

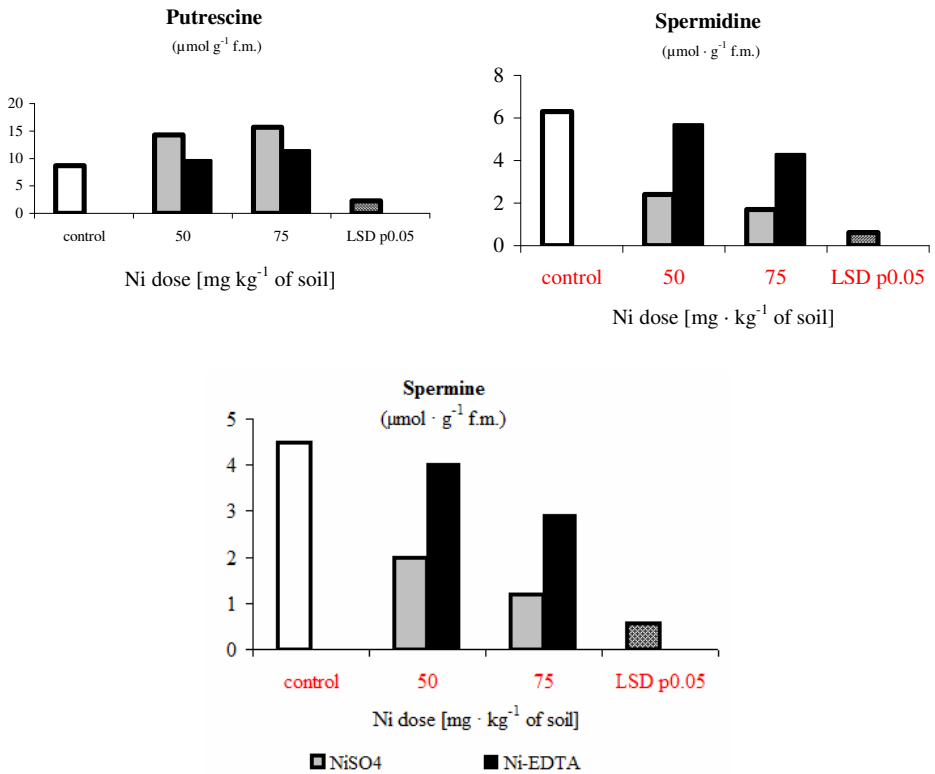

Fig. 1. The comparison of polyamines content in leaves of barley plants grown in the presence of inorganic and chelatic nickel excess, LSD p0.05 - the least significant difference with a probability of 0.05

In spite of the fact that putrescine has the ability of inactivating free radicals generated in cells of plants exposed to heavy metal stress [5], it is generally considered to be a hormone which causes plant ageing because it speeds up the apoptosis of cells [8, 18]. Moreover, it has been shown that in stress conditions, parallel to accumulation of putrescine, such unfavourable consequences of stress as depolarisation of membranes, effect of potassium ions, a drop in protein content as well as withering and necrosis of plant

organs can be observed [8]. In the conducted experiment the level of putrescine corresponded to morphological symptoms of nickel toxicity, such as leaf chlorosis and necrosis. These symptoms appeared at the top of the youngest leaves when the soil was contaminated with inorganic nickel, ie when the largest increase in putrescine content was observed.

Studies conducted so far have shown that the mechanism of nickel toxicity is connected with initiation of free-radical reactions *in vivo*, including lipid peroxidation of cell membranes [19, 20]. Studies conducted so far have also shown that polyamines, including putrescine, takes part in inactivating free radicals [5, 9]. A larger increase in the content of this polyamine, which was observed in the presence of nickel sulphate, as compared with the increase noted in the presence of Ni-EDTA chelate, suggests that inorganic nickel induced a stronger oxidative stress in the cells of barley leaves than Ni-EDTA chelate. The difference could result from a different content of this metal *in vivo.* Earlier studies showed that spring barley cv. Poldek assimilated more nickel from acid soil contaminated with the sulphate form of this metal than with Ni-EDTA [21].

Studies conducted so far have also shown that there are differences in the level of spermine and spermidine in barley leaves grown in the presence of inorganic and chelatic form of nickel (Fig. 1). The level of these polyamines was markedly lower in the presence of $NiSO_4$ than in the presence of Ni-EDTA. These differences could result from different phytoassimilation of this element from the two chemical forms.

Studies conducted so far have shown that in stress conditions spermine and spermidine protect cytoplasmic membranes [10-12]. According to Roberts et al [10] spermine and spermidine associate with the surface of membranes, stabilizing their permeability. Results (to be published in Ecol. Chem. Eng.) obtained by the authors show that the level of these two polyamines correlates negatively with the degree of damage to membranes, measured by the content of MDA *in vivo* and the outflow of electrolytes from plant tissues.

Conclusion

In stress conditions caused by inorganic ($NiSO_4 \cdot 7H_2O$) and chelate (Ni-EDTA) forms of nickel the metabolism of polyamines in leaves of spring barley cv. Poldek changed. The direction of the changes in the metabolism of these compounds was specific to this metal and did not depend on the chemical form in which it was applied to the soil; the content of putrescine increased, whereas the content of spermine and spermidine decreased. However, intensity of metabolism of polyamines depended on the chemical form in which nickel was applied to the soil. In the presence of excess of inorganic nickel ($NiSO_4 \cdot 7H_2O$) an increase in the content of putrescine and a decrease in the content of spermine and spermidine in barley leaves were much bigger than in the presence of excess of chelatic nickel (Ni-EDTA).

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PORÓWNANIE ZAWARTOŚCI POLIAMIN W LIŚCIACH JĘCZMIENIA UPRAWIANEGO W WARUNKACH STRESU POWODOWANEGO PRZEZ NIKIEL W FORMIE NIEORGANICZNEJ I CHELATOWEJ

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Abstrakt: W doświadczeniu wazonowym zbadano wpływ niklu na metabolizm poliamin w liściach jęczmienia jarego odmiany Poldek. Nikiel aplikowano do gleby kwaśnej w formie $NiSO_4 \cdot 7H_2O$ oraz Ni-EDTA (M:L 1:1), w dawkach 50 i 75 mg Ni $\cdot$ kg^{-1} gleby. Po 10-dniowej ekspozycji roślin na działanie obu form chemicznych niklu zwiększyła się zawartość putrescyny, a obniżyła zawartość sperminy i spermidyny w liściach jęczmienia. W warunkach stresu powodowanego przez siarczan niklu zarówno poziom wzrostu zawartości putrescyny, jak i obniżenia sperminy i spermidyny w liściach był znacznie większy niż w warunkach stresu powodowanego przez chelat Ni-EDTA.

Słowa kluczowe: jęczmień jary, spermidyna, spermina, stres niklowy, putrescyna

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PHYTOTOXIC EFFECT OF SOME METAL IONS ON SELECTED RAPESEED CULTIVARS REGISTERED IN SLOVAKIA

WPŁYW FITOTOKSYCZNOŚCI JONÓW NIEKTÓRYCH METALI NA WYBRANE ODMIANY UPRAWNE RZEPAKU ZAREJESTROWANE NA SŁOWACJI

Abstract: The aim of this study was to investigate the phytotoxic effects of seven metal ions (Cd(II), Cr(VI), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II)) on length of roots of five rapeseed (*Brassica napus* L. *subsp. napus*) cultivars registered in Slovakia (Atlantic, Baldur, Californium, Oponent and Verona). The phytotoxic effect of metals was evaluated using IC_{50} values. The studied metal ions inhibited germination and root growth of rapeseed seedlings. In general, the toxicity of metal ions decreased in the following order Cu > Cr >Hg > Cd > Pb > Ni > Zn. Atlantic, Baldur and Californium were more sensitive to Cd than to Ni, for Oponent and Verona higher toxicity exhibited Ni. From the studied rapeseed cultivars Atlantic and Californium were found to be most sensitive to tested metals. On the other hand, high tolerance to metal treatment was determined for Baldur. Czech cultivar Opponent showed high tolerance to Cd, Cr, Cu and Pb, but it was sensitive to Hg and Ni. The above-mentioned results confirmed differences in the metal tolerance of tested rapeseed cultivars.

Keywords: toxic metals, *Brassica napus* L., phytotoxicity, root growth

Rapeseed (*Brassica napus* L. *subsp. napus*) is the most important oil crop in Slovakia with a wide spectrum of utilization: as an agricultural crop (food industry), worthful nutritive animal fodder (rapeseed press cakes) and technical crop. From rapeseed oil biocomponent FAME for biodiesel is prepared [1, 2]. Some *Brassica* species (*Brassica napus* and *Raphanus sativus)* showed a moderate tolerance against several metals and thus, rapeseed can be used for remediation of soils contaminated by toxic metals [3, 4]. If soils contaminated with heavy metals are phytoremediated by oil crops (such as *Brassica* ssp.), biodiesel production from the resulting plant oil could be a viable option to generate bioenergy [5].

Elongation growth is a complex process including turgor changes, synthesis of cell membrane components and content of growth regulators. Excess of heavy metals inhibits elongation plant growth [6, 7]. Some authors consider that inhibition of the cell cycle is the basis for growth inhibition [8]. Moreover, many toxic metal ions are efficient catalysts in the formation of several reactive oxygen species and other free radicals which adversely affect physiological processes in plants, including plant growth [6, 9].

Uptake of toxic amounts of metal by higher plants or algae can result in inhibition of several enzymes and in increase in activity of others. Metal accumulation in the cellular compartment is a prerequisite for enzyme inhibition *in vivo.* Binding of toxic metals to sulfhydryl groups, involved in the catalytic action of structural integrity of enzymes results in inhibition of enzyme activity. On the other hand, the induction of some enzymes (eg

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SOD, CAT, etc.) is considered to play a significant role in the stress metabolism, induced by metal phytotoxicity [10].

This study is aimed to investigate the effect of seven metals ions (Cd(II), Cr(VI), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II)) on root growth of five cultivars of *Brassica napus* plants registered in Slovakia (Atlantic, Baldur, Californium, Oponent and Verona) and to determine differences in intraspecific sensitivity of rapeseed to metal induced stress.

Material and methods

For experiments following compounds were used: $Cd(NO_3)_2 \cdot 4H_2O$, $K_2Cr_2O_7$, $CuCl_2 \cdot 2H_2O$, $HgCl_2$, $NiCl_2 \cdot 6H_2O$, $Pb(NO_3)_2$ and $ZnCl_2 \cdot H_2O$. These analytical reagent-grade chemicals purchased from Lachema (Brno, Czech Republic) were employed for the preparation of all solutions.

For experiments seeds of following five rapeseed cultivars registered in Slovakia were used: Atlantic, Baldur, Californium, Oponent and Verona. The seeds were purchased from Slovak Centrum of Agricultural Production, Research Institute of Plant Production in Piestany, Slovakia. Atlantic is a medium-early and high type genotype suitable for potato production region; Baldur is a medium-early and medium-high type of genotype suitable for all production regions; Californium is a medium-early to early and medium-high type of genotype suitable for maize production region; Oponent is a late and high type of genotype suitable for potato production region and Verona is a late and medium-high genotype suitable for maize and potato production regions [2, 11].

The seeds of *Brassica napus* were placed in Petri dishes with a 14 cm diameter and filter paper on the bottom. In each Petri dish 58 seeds were evenly displayed on the surface of filter paper and the amount of solution used was 10 cm^3 per dish. Each concentration was duplicated. After 72 hours exposure at mean air temperature (25ºC) in the dark the length of roots and shoots was measured. The applied concentration range of studied compounds was 10^{-6} to 10^{-3} mol dm^{-3}.

Results and discussion

Previously it was found that rapeseed is a suitable plant species for investigations of metal phytotoxicity [12]. In the present study *root tolerance index* (RTI) was calculated as the mean seminal root length in the metal treatment divided by the mean seminal root length in the control. From the dependence of RTI on the concentration of applied toxic metals IC_{50} values, ie molar concentrations of the studied metals causing a 50 % inhibition of the studied parameter, were determined (Table 1).

In general, the toxicity of metal ions decreased in the following order Cu > Cr >Hg > Cd > Pb > Ni > Zn. Atlantic (A), Baldur (B) and Californium (C) were more sensitive to Cd than to Ni, for Oponent (O) and Verona (V) higher toxicity exhibited Ni. The sensitivity of studied cultivars treated with toxic metals decreased as follows: for Cd: A > C > V > B > O; for Cr: A = C = V > B = O; for Pb: A > V > C > B > O, for Zn: A > C > O > V > B, for Cu: A > C = V > B > O , for Hg: O > C > A = V > B and for Ni: O = A >V > B > C. Thus, it can be concluded that from the studied rapeseed cultivars Atlantic and Californium were found to be most sensitive to tested metals. On the other hand, overall high tolerance to metal treatment was determined for Baldur. Czech cultivar Opponent showed high tolerance to Cd, Cr, Pb and Cu but it was sensitive to Hg and Ni.

Table 1

IC_{50} values related to root growth inhibition of five rapeseed cultivars by tested metals (C.L. - *confidence limits*)

Metal	$IC_{50} \pm C.L._{0.05}$ [mmol dm^{-3}]				
	Atlantic	**Baldur**	**Californium**	**Oponent**	**Verona**
Cd	**0.554** 0.295÷1.090	**0.659** 0.320÷1.47	**0.571** 0.200÷1.912	**0.684** 0.427÷1.180	**0.615** 0.353÷1.150
Cr	**0.114** 0.056÷0.264	**0.122** 0.048÷0.400	**0.114** 0.060÷0.252	**0.124** 0.060÷0.308	**0.128** 0.054÷0.324
Cu	**0.065** 0.037÷0.125	**0.088** 0.061÷0.145	**0.071** 0.039÷0.146	**0.089** 0.047÷0.208	**0.072** 0.036÷0.192
Hg	**0.392** 0.222÷0.742	**0.539** 0.230÷1.542	**0.375** 0.175÷0.826	**0.369** 0.237÷0.588	**0.396** 0.192÷0.878
Ni	**0.609** 0.443÷1.078	**0.644** 0.379÷1.142	**0.748** 0.488÷1.204	**0.607** 0.428÷0.868	**0.612** 0.359÷1.084
Pb	**0.581** 0.299÷1.261	**0.736** 0.376÷1.575	**0.701** 0.416÷1.240	**0.880** 0.644÷1.241	**0.696** 0.351÷1.480
Zn	**0.803** 0.404÷1.863	**1.168** 0.808÷1.757	**0.834** 0.410÷1.905	**0.850** 0.576÷1.347	**1.130** 0.596÷2.287

Toxic effect of metal ions depends on their physico-chemical properties. Nieboer and Richardson [13] classified metals based on their ionic and covalent bonding tendencies and donor-atom preference of metals. These authors used the dependence of the covalent index *versus* the ionic index as a base for classification of metal and metalloid ions to three classes. Metals of class A are oxygen donor-atom seekers, whereas those of class B are nitrogen and sulphur seekers and metals ranged to borderline metals are characterized by ambivalent affinity for all three donor-atom. According to Nieboer et al [14] from the investigated seven metals Hg^{2+} was classified as a metal of class B, the other ones as borderline (intermediate) metals. On the other hand, Duffus [15] assigned Cd^{2+} and Pb^{2+} to the metals of class B.

Ivanov et al [16] investigated the effect of different metal ions on root growth inhibition of maize plants and found that the inhibitory effectiveness decreased in the following order: $Cu^{2+} > Hg^{2+} > Cd^{2+} > Zn^{2+}$ and the IC_{50} values related to the inhibition of root growth showed correlation with the affinity of metal ions to –SH groups. The rank of inhibitory effectiveness for phytotoxic effects of above metals on maize roots was the same as determined in our experiment for rapeseed plants. It is known that toxic metals act as mitotic inhibitors what is reflected in the reduction of root growth. Jiang et al [17] observed toxic effect of $CuSO_4$ ($10^{-4} \div 10^{-2}$ mol dm^{-3}) on the morphology of chromosomes. Doncheva [18] found that copper interrupts the nuclei formation at the crucial- G_1/S transition point of the cell cycle, when it prevents their entry into mitosis. Reduced root growth could be connected with copper effect on proliferation of root meristem cells. Yadav and Srivastava [19] confirmed inhibitory effect of Cd^{2+} ions on mitotic index as well as on active mitotic index for *Hordeum vulgare* and *Setaria italica.* These authors observed different types of mitotic aberration due to Cd^{2+} action. Ni^{2+} ions belong to strong mitotic inhibitors causing modification on membrane permeability, inhibition of ascorbate peroxidase. However, these negative effects could be reduced by synthetic cytokinins [20].

Summarizing the obtained results it can be concluded that root tolerance index (RTI) was found to serve as good biomarker for evaluating the relative toxicity of toxic metals to rapeseed cultivars.

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POLYCARBONATE COMBUSTION IN A FLUIDISED BED REACTOR

SPALANIE POLIWĘGLANU W REAKTORZE FLUIDYZACYJNYM

Abstract: In the article there is some results of the realized experiments of some polycarbonate combustion in the laboratory fluidised bed reactor. The thermal utilization processes enable the total removal of the waste plastics from the environment with simultaneously the useable energy recovery possibility. The chemical composition of polycarbonate makes the thermal decomposition processes very difficult. The thermal decomposition of polycarbonate, as the high oxygen index plastic, requires some specific conditions of the process operation in order to the complete oxidation realization and the prevention of the emissions of some toxic substances into the atmosphere. The turbulence, the oxygen presence in the reaction zone and the high temperature of the fluidised bed ensure the favourable conditions of the thermal decomposition process in fluidised bed reactors. The combustion processes of this waste plastic may be a useable alternative energy source. The aim of the realized experiments is the examination of the polycarbonate combustion process parameters in fluidised bed reactors and the elaboration of the principal technological conditions of the thermal decomposition process.

Keywords: polycarbonate combustion, thermal decomposition, fluidised bed reactor

Polycarbonate is a synthetic thermoplastic polymer that is mainly produced by the polycondensation of bisphenol A with phosgene. Polycarbonate physical properties (transparency, mechanical strength and dielectric properties) make wide applications possible. It is used as an engineering plastic and probably the most meaningful parts of its production are for electrical and electronic industry (sockets, plugs, connectors, loudspeakers, electrical insulations, lamp enclosures, mobile phone enclosures), and also medical instruments (blood oxygenators, dialysis machines, optical glasses and diverse kinds of lenses) and automotive industry (automotive windows and lights, motorcycle windshield visors and helmets, streetlights, traffic signals). It is commonly used in lots of laboratory equipment (flash-light instruments, microscope parts, tubes, rods) and domestic utensils (electrical kettles, coffee makers, electrical grills, microwave ovens and other kitchen dishes and some package containers and also electric shavers, hair-dryers, tanks for flat irons) and some specific data carriers (identity cards, credit cards, compact discs and digital versatile discs). The polycarbonate, like most organic synthetic polymers, is built from carbon, hydrogen and oxygen atoms (the mass fraction of C : H : O = 0.756 : 0.055 : 0.189) and the average molecular weight of one macromolecule in the polymer structure can be equal form 25 000 to 75 000 and even 100 000. Polycarbonate is an amorphous polymer but partial crystalline forms can be also manufactured. The polymer melts when heated to 230ºC and when the temperature is above 320ºC it begins to decompose and the most efficient destruction process occur when the temperature is about 550ºC. The energy from the broken chemical bonds is released [1-6]. Bisphenol A polycarbonate presents good

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resistance to burning even without flame-retardant additives, it has an oxygen index (OI) of 26 and is listed as V-2 by Underwriters' Laboratory [7]. All the substances that are used to the considered polymer production (phosgene, bisphenol A - a condensation product of acetone and phenol) are not neutral to human health, so if the polycarbonate decomposition is possible, the waste polycarbonate wares should be properly utilized.

Combustion is a process of a high temperature oxidation. During this process the chemical compounds are destroyed with some new substances creation. The basic products of the complete combustion of the chemical compounds that are built from carbon, hydrogen and oxygen atoms are carbon dioxide and water vapour [8]. In fact any kind of combustion is a very complicated process with a sequence of intermediate steps and not always the complete combustion products are created in the first combustion zone. The most harmful incomplete combustion products, mainly including carbon monoxide and volatile organic compounds, have to be oxidized in the next combustion zone, what is practically applied in industrial combustion plants and waste incinerators [9].

Fluidised bed reactors are very favourable devices for thermal utilization of diverse kinds of waste [10, 11]. In industrial fluidised bed reactors the chemically inert or active bed is fluidised by some air and the combustible substances are mixed with the fluidised bed and with the air which is the oxygen source. When the considered burned substances are relatively resistant to decomposing, and thus difficult to oxidizing, then the hot fluidised bed particles heat these substances up and facilitate and accelerate their thermal decomposition.

Concerning all the previous mentioned facts, the utilization of waste polycarbonate wares in fluidised bed reactors was proposed as the applicable method of the thermal disposal of this plastic from the environment. Plastics are very common solid municipal waste components. Their wide applications contribute to the presence of them in almost all kinds of waste. Nowadays a great deal of waste is burned in industrial incineration plants as a result of the obligatory policy [9] and the special care have to be imposed to the prevention of the emissions of some toxic substances into the atmosphere. The benefits will enclose the whole environment.

Experimental data and discussion

The experiments of the thermal decomposition of some bisphenol A polycarbonate, which chemical structure is in Figures 1 and 6, were carried out in the laboratory bubbling fluidised bed reactor - schematically presented in the Figure 2. The experiments were realized as the combustion process of some polycarbonate samples with propane, a high calorific saturated aliphatic hydrocarbon that was used to the maintenance of the appropriate temperature conditions.

The whole laboratory site consisted of the fluidised bed reactor itself and the accompanying operating, controlling and measuring devices. The reactor was the vertical oriented cylindrical quartz tube of the height 500 mm and the diameter 96 mm and it rested on the flat perforated Cr/Ni steel distributor. The total amount of the circular holes in the distributor was equal to about 450 and their diameters were equal to 0.6 mm. The air and the propane were supplied to the reactor plenum chamber by the separate pipes with each gas flux controlling, the stream of air was equal to 1.650 dm^3/s and the stream of propane was equal to 0.046 dm^3/s resulting in the 50% of the air excess.

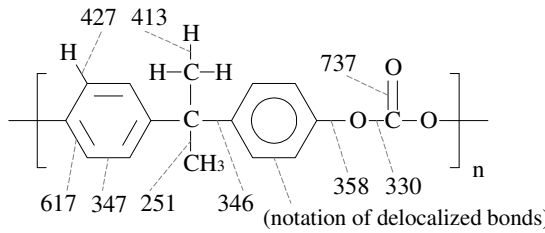

Fig. 1. The bisphenol A polycarbonate bond dissociation energies [kJ/mol] [4]

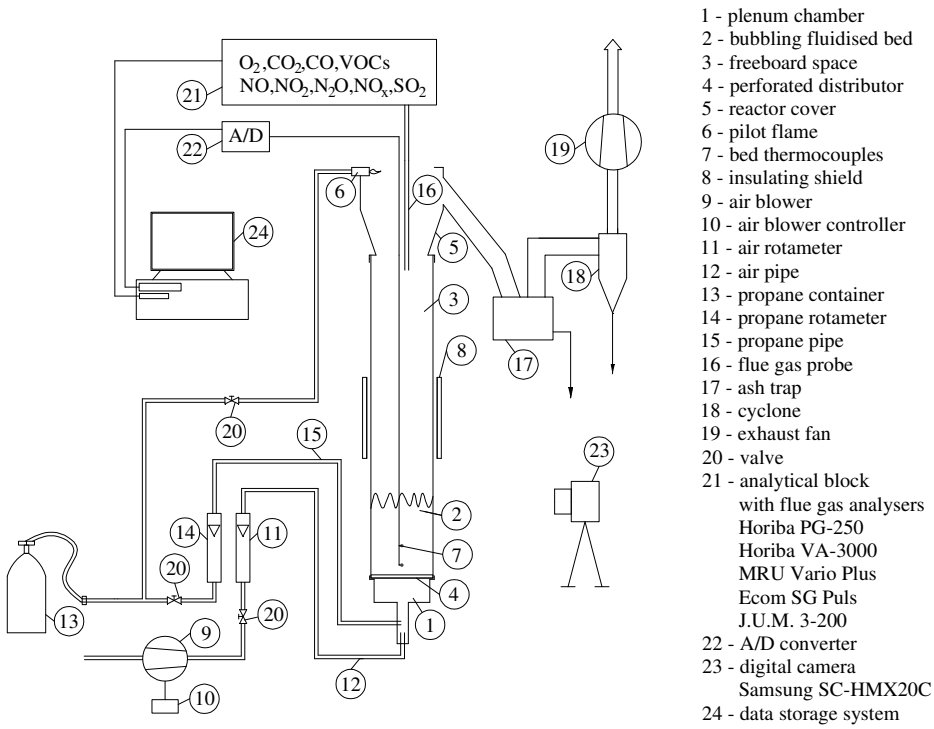

Fig. 2. The scheme of the laboratory fluidised bed reactor

The hydrocarbon fuel was burned in the reactor bed and the exothermic combustion reactions heated the fluidised sand bed up. The total mass of the quartz sand particles was equal to 300 g and the diameters of the sand particles were about from 0.385 to 0.430 mm. While the realization of the main stages of the experiments, the temperature of the sand bed measured by two Cr/Ni-Ni thermocouples located 20 and 50 mm above the distributor was equal to 900ºC or even 960ºC when the insulating shield covered a part of the reactor tube. The exhaust pipe was localized at the top of the reactor and the flue gases were transported through the ash trap and the cyclone and were taken out from the reactor by the operation of the exhaust fan which released them into the atmosphere. The concentrations of the selected

components in the flue gases were monitored by using special technically available methods and the digital camera was used to take some photos (Figs 3-5).

Fig. 3. The fluidised bed reactor just after the ignition of propane–air mixture (bed temperature 400ºC)

Fig. 4. The fluidised bed combustion of propane (bed temperature 900ºC)

Fig. 5. The fluidised bed combustion of propane with some polycarbonate sample (bed temperature 900ºC)

The analytical block of the laboratory site included four gas analyser devices that applied different analytical methods:

- Ecom SG Plus gas analyser: O_2, CO, NO, NO_2, SO_2 (electrochemical method)
- MRU Vario Plus gas analyser: O_2, CO, NO, NO_2, SO_2 (electrochemical method), CO_2 and the sum of volatile organic compounds (infrared radiation method)
- Horiba VA-3000 and PG-250 gas analysers: CO_2, CO, N_2O, SO_2 (infrared radiation method), O_2 (electrochemical method), NO, NO_x (chemiluminescent acid method)
- J.U.M. 3-200 gas analyser: total volatile organic compounds (flame ionization detector method)

and Samsung SC-HMX20C digital camera enabled to take 250 pictures per second (336 pixels x 448 pixels).

It was observed that while the thermal decomposition of some polycarbonate samples in the fluidised bed reactor, as contrasted with only propane combustion, some flames were present. The flames appeared in the bed and they came to the reactor freeboard space where they vanished gradually. The careful observations allowed to state that the whole process started in the hot fluidised sand bed where the vapour bubbles around each polycarbonate

particle were created. The vapour bubbles were supposed to consist of the polycarbonate pyrolysis products.

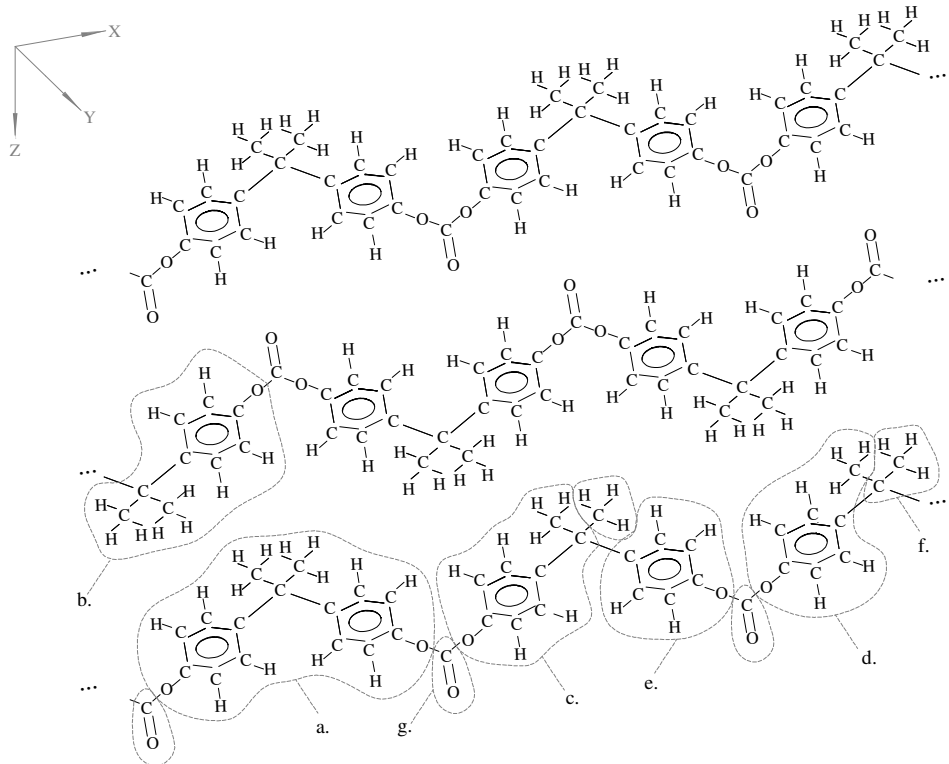

Fig. 6. The polycarbonate structure and the suggested scheme of the formation of some polycarbonate pyrolysis products: a) bisphenol, b) 4-propylphenol, c) 4-ethylphenol, d) 4-methylphenol, e) phenol, f) hydrocarbon, g) carbon monoxide, in a) to e) 'sub-pictures' the broken bonds need some hydrogen atoms for the suggested chemical compounds formation, the hydrogen atoms are present in f) and the rested carbon atoms from f) could be easily oxidized in combustion processes, the chemically bonded carbon atoms could also create some polycyclic carbon structures

The suggested scheme of the formation of some polycarbonate pyrolysis products is schematically presented in Figure 6. During the pyrolysis process the chemical bonds are usually broken in the sequence form the lowest to the highest bond dissociation energies. It was notices that after the diameters of the bubbles in the bed achieved about 20 mm, the pyrolysis products started to come from the fluidised bed, so some specific volume of the pyrolysis products was needed before these substances could be ignited by the surrounded combustible propane - air mixture and then could be oxidized. Probably the concentrations of the hydrocarbon radicals in the vapour bubbles were then sufficient to start the combustion process of the other pyrolysis products. The diffusion of oxygen to the pyrolysis products in the freeboard space contributed to the total disappearance of the

blazing flames before the exhaust gases entered into the flue gas probe. As a consequence nearly 100% of the carbon atoms that were built into the polymer structure turned into carbon dioxide molecules, the mass fractions of the monitored incomplete combustion products (CO and VOCs) in the flue gases were negligible. Despite this fact, the shining flames were the proof of the formation of some polycyclic aromatic hydrocarbons in the flue gases what contributed to the creation of some soot that covered the reactor quartz tube. The absence of some proper thermal insulation made a complete combustion process very difficult.

The combustion is a sequence of lots of radical reactions and the proceeds of them depend on the combustion process conditions, such as temperature, pressure and the kinds and the concentrations of the combustible mixture components. In case of polycarbonate with propane combustion the possible radical reactions include aliphatic hydrocarbon fuel oxidation processes and the reactions of the conversions and the destructions of the aromatic rings. There are many stages of the whole process and the great number of the reactions makes the precise studies very difficult. The crucial issue for the combustion processes of hydrocarbon fuels is the presence of such radicals as: $^{\bullet}H$, $^{\bullet}O$, $^{\bullet}OH$ and $^{\bullet}CH_x$ in the gaseous reactivity zone. Some possible reactions during combustion of polycarbonate with propane are proposed below [8, 12]:

The radicals $^{\bullet}H$, $^{\bullet}O$, $^{\bullet}OH$ may be produced at high temperature by the destruction of the molecules while the collisions with the hot reactor walls:

$$^{\bullet}H + O_2 \rightarrow {}^{\bullet}O + {}^{\bullet}OH \quad (1)$$

$$^{\bullet}O + H_2 \rightarrow {}^{\bullet}H + {}^{\bullet}OH \quad (2)$$

$$^{\bullet}OH + H_2 \rightarrow {}^{\bullet}H + H_2O \quad (3)$$

The aliphatic hydrocarbon (propane) is decomposed by the abstraction of the hydrogen atoms and then the intermediate products are gradually oxidized:

$$C_3H_8 + (^{\bullet}H, {}^{\bullet}O, {}^{\bullet}OH) \rightarrow i\text{-}C_3H_7 + (H_2, {}^{\bullet}OH, H_2O) \quad (4)$$

$$i\text{-}C_3H_7 \rightarrow i\text{-}C_3H_6 + {}^{\bullet}H \quad (5)$$

$$C_3H_6 + {}^{\bullet}O \rightarrow {}^{\bullet}C_2H_5 + {}^{\bullet}CHO \quad (6)$$

$$^{\bullet}C_2H_5 + {}^{\bullet}CHO \rightarrow CH_2CO + {}^{\bullet}CH_3 + {}^{\bullet}H \quad (7)$$

$$CH_2CO + {}^{\bullet}O \rightarrow CH_2O + CO \quad (8)$$

$$^{\bullet}CH_3 + {}^{\bullet}O \rightarrow CH_2O + {}^{\bullet}H \quad (9)$$

$$CH_2O + {}^{\bullet}O \rightarrow {}^{\bullet}CHO + {}^{\bullet}OH \quad (10)$$

$$^{\bullet}CHO + {}^{\bullet}O \rightarrow CO + {}^{\bullet}OH \quad (11)$$

$$CO + {}^{\bullet}OH \rightarrow CO_2 + {}^{\bullet}H \quad (12)$$

While combustion of polycarbonate lots of phenoxy radicals are present because of the decomposition of the bisphenol groups. The process of the detachment of the methyl groups from the bisphenol groups proceeds easier than the destruction of the ring structures. The delocalized bonds make the ‘rings’ relatively thermally resistant.

In Figure 7 there is a sequence of the reactions during the phenoxy radical oxidation represented and in Figure 8 the mechanism of the polycyclic aromatic hydrocarbon growth

is illustrated. The presence of the ring structures in the reactionary combustion zone makes the greater possibility to some soot creation.

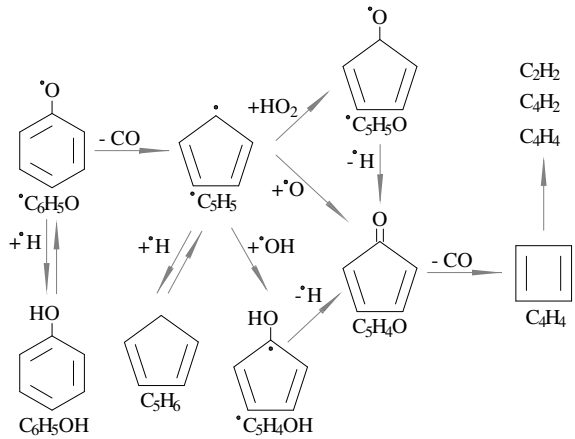

Fig. 7. The pathways of the reactions during the phenoxy radical oxidation [8]

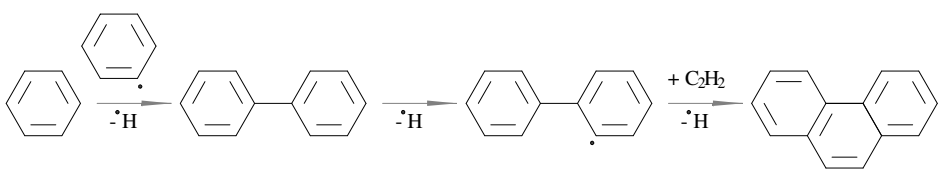

Fig. 8. The mechanism of the polycyclic aromatic hydrocarbon growth [8]

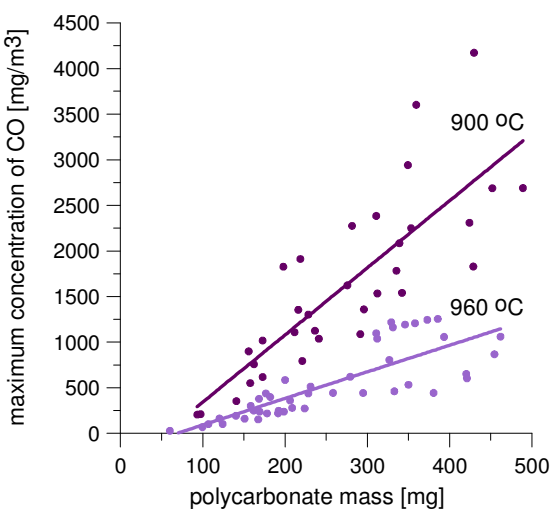

Fig. 9. The maximum concentrations of the emitted carbon monoxide in the flue gases versus the masses of the burned polycarbonate samples in 960 and 900ºC

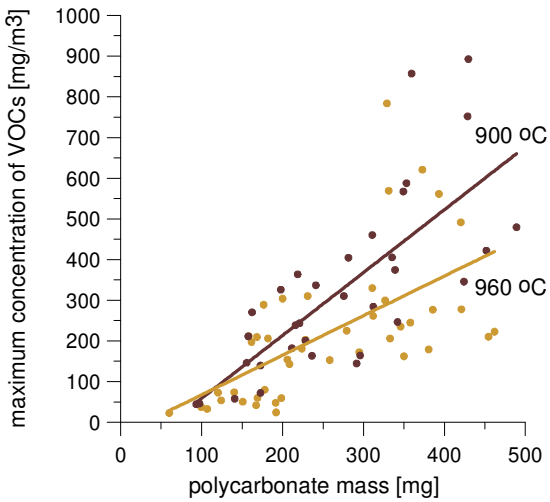

Fig. 10. The maximum concentrations of the emitted volatile organic compounds in the flue gases versus the masses of the burned polycarbonate samples in 960 and 900ºC

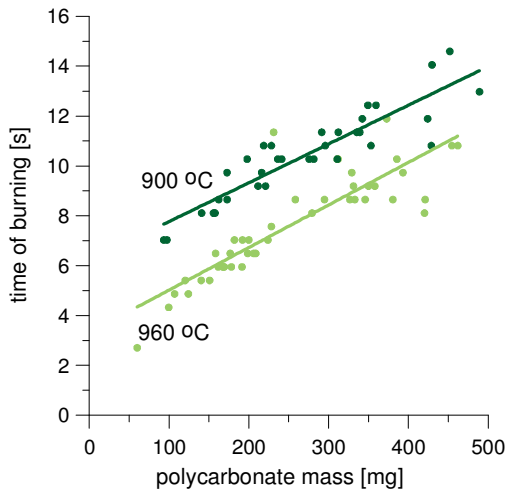

Fig. 11. The duration of the burning process of the polycarbonate samples in 960 and 900ºC (four particles in each sample)

The experiments that were carried out in the different temperature conditions and with the different quantity of the polycarbonate particles thrown into the hot fluidised sand bed simultaneously allowed to draw some conclusions. The higher temperature contributed to the better progress of the oxidation reactions and thus the lower emissions of the incomplete combustion products were observed then. While the thermal decomposition of some polycarbonate samples in the higher temperature conditions (960ºC), the maximum emission values of carbon monoxide and volatile organic compounds in the flue gases were lower, if comparing to these emission values in the lower temperature conditions (900ºC).

In the higher temperature conditions the thermal decomposition process of the analysed polymer proceeded quicker because the time of burning of the same polycarbonate mass was shorter. The thermal decomposition processes of all the polymer particles, that created one polycarbonate sample, proceeded independently and that is way the same time was needed for the greater total polycarbonate mass burning when the sample consisted of the greater numbers of the particles. In other words, when the polymer particle was smaller, resulting in smaller particle mass, then the whole burning process took shorter. All the mentioned facts were presented in Figures 9-12 and they arise from the combustion process kinetics.

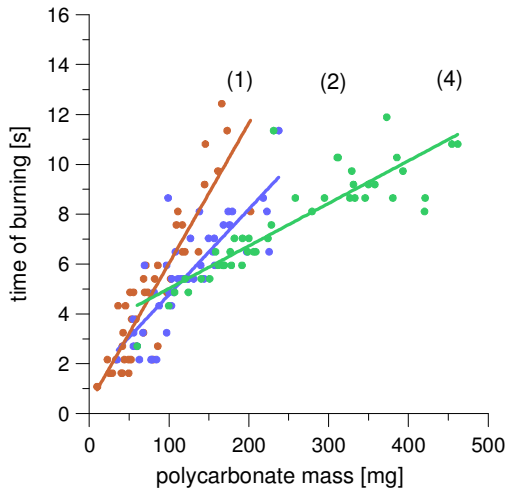

Fig. 12. The duration of the burning process of the polycarbonate samples consisted of the different quantities of the particles (bed temperature 960ºC)

The maximum values of the emissions of the incomplete combustion process products are important because when fuels or waste are burned in combustion plants or incineration plants, the values of the emissions that must not be exceeded are given in the obligatory laws as the maximum concentrations of some substances in the exhaust gases [13, 14]. The total amounts of carbon monoxide and volatile organic compounds depended on the process conditions and the mass of the burned polycarbonate but the concentrations of the pollutants in the flue gases are measured in industrial combustion plants or thermal waste utilization systems. The proper process conditions could ensure low emissions of harmful pollutants.

Conclusions

In most aliphatic hydrocarbons the molar ratio of carbon atoms to hydrogen atoms is about a half what contributes to the specific combustion conditions with lots of radicals. In aromatic hydrocarbons there is often more carbon atoms than hydrogen atoms and the carbon atoms are bonded in ring structures which create the relatively strong chemical structures. These facts are meaningful when pyrolysis and oxidative reactions during combustion processes are considered. Polycarbonate, as a polymer with a lot of aromatic

bonds in its structure, is very resistant to thermal decomposition processes and it is also susceptible to forming some pollutants during thermal utilization [15]. The laboratory fluidised bed reactor with the continuous mixing of the burned substance with the air excess and some high calorific aliphatic hydrocarbon fuel in the atmosphere of the hot chemically inert material (quartz sand) ensured the specific conditions for the thermal decomposition processes.

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SPALANIE POLIWĘGLANU W REAKTORZE FLUIDYZACYJNYM

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Abstrakt: Przedstawiono wyniki eksperymentów spalania poliwęglanu w laboratoryjnym reaktorze fluidyzacyjnym. Procesy termicznej utylizacji umożliwiają całkowite usunięcie odpadowych tworzyw sztucznych ze środowiska przy jednoczesnej możliwości odzysku energii. Budowa chemiczna poliwęglanu utrudnia prowadzenie procesów termicznego rozkładu. Rozkład termiczny poliwęglanu, jako tworzywa sztucznego o wysokim indeksie tlenowym, wymaga specyficznych warunków prowadzenia procesu w celu możliwości realizacji całkowitego utlenienia oraz uniknięcia emisji szkodliwych substancji do atmosfery. Turbulencja, obecność tlenu w strefie reakcji oraz wysoka temperatura fluidyzującego złoża zapewniają korzystne warunki prowadzenia procesu termicznego rozkładu w reaktorach fluidyzacyjnych. Procesy spalania odpadowych tworzyw sztucznych mogą stanowić użyteczne źródło alternatywnej energii. Celem realizowanych eksperymentów jest zbadanie parametrów spalania poliwęglanu w reaktorach fluidyzacyjnych oraz opracowanie zasadniczych technologicznych warunków procesu termicznego rozkładu.

Słowa kluczowe: spalanie poliwęglanu, termiczny rozkład, reaktor fluidyzacyjny

Terese RAUCKYTE-ŻAK[1]

ATTEMPTS OF MATHEMATICAL MODELLING TO ACCESS GENERAL TOXICITY OF METAL CONTAINING WASTES

PRÓBY MODELOWANIA MATEMATYCZNEGO NA POTRZEBY OGÓLNEJ OCENY TOKSYCZNOŚCI ODPADÓW ZAWIERAJĄCYCH METALE

Abstract: Attempts to make preliminary assessment of general toxicity of metal containing wastes, including heavy metals in the first place, were made by using a polynomial, static and at the same time predictive mathematical model. The general toxicity was defined for samples of wastes, where metals were determined by using *toxicity characteristic leaching procedure* (TCLP). Gradient factors (a, b, c, …, n) for an equation for general toxicity in the form of $y(x_1, x_2, x_3, \ldots, x_n) = ax_1 + bx_2 + cx_3 + \ldots + nx_n$ were selected with the use of weighted average, considering the contents of the individual metals and their toxicological properties. Seeking the assessment criterion, it was assumed that the contents of metals leached from the tested wastes in toxic concentrations may be hazardous for the components of biosphere when the value of total toxicity fulfils the relation: $y(x_1, x_2, x_3, \ldots, x_n) \geq 1$. The magnitude of general toxicity (y) was calculated by summation of the experimentally determined individual concentrations of elements, taking into account their weighted fraction in the total toxic load. Basing on computing for the assumed model of general toxicity for selected wastes and considering the verification of the model with reference to the toxicity criteria defined in TCLP, it was found that there existed the coincidence of the achieved results.

Keywords: general toxicity assessment, mathematical modelling, metals with toxic concentrations

In literature, you can find two basic attempts to solve the issue of mathematical modelling of natural systems that exist in ecosystems [1]. With the use of the so-called descriptive and prognostic or predictive approach, there are attempts to present mathematically the abstract systems in the way that is the most similar to the actual world. The aim of the descriptive approach is to use the mathematical model to achieve the largest amount of information about the way how the actual system functions, in other words, to obtain the results of modelling with reference to basic experimental data. In case of predictive modelling, the main purpose is to obtain the most likely and representative experimental results describing a given phenomenon to use them as input data for the abstract mathematical modelling. At present, the most popular are predictive models [2]. For instance, the Langmuir and Freundlich sorption models are typical predictive models used eg to describe events of sorption of pollutants in soil and sediments or sludge. They are most highly valued due to the fact that they properly match a theoretical adsorption curve to the experimental data [3]. In literature, you can find much more descriptive approach to the phenomenon of heavy metals sorption in water-soil environment. Sorption on mineral and organic fractions is the most recognised and the most frequently determined. The sorption on mineral fractions are described, among others, by the following models: *Constant Capacitance Model* (CCM), *Diffuse Layer Model* - (DLM), *Triple Layer Model* (TLM), or *Three Plane Model* (TPM). The most frequently used are: CCM, DLM and TLM, which were included into the geochemical speciation code MINTEQ2, also in its complemented and enhanced form: MINTEQ3 [4, 5]. In literature,

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you can find works concerning mathematical modelling of remediation soils contaminated with heavy metals [6], transport of metals from soil to deciduous trees [7], phytoextraction with eg maize [8], and simulation of the metal mobility in soils contaminated with sewage sludges [9]. Moreover, the literature raises the issues of bioaccumulation of metals in sea benthic deposits [10] or in oceans by comparing complex models with eg a toxicokinetic one [11].

Computational part

Standardised values for metals from the TCLP (*toxicity characteristic leaching procedure*) were used to pre-assess the general toxicity of wastes in a static (ie: not including variations in values in time) predictive and polynomial model in the form:

$$y(x_1, x_2, x_3, \ldots, x_n) = ax_1 + bx_2 + cx_3 + \ldots + nx_n \quad (1)$$

where: y - general toxicity of the tested waste [mg/dm^3]; a, b, c, …, n - weighted conversion factors of limit values of metal concentration in the TCLP criterion (considering toxicological properties); x_1, x_2, x_3, …, x_n - independent variables which present values of determined concentrations for the individual metals in wastes samples acc. to TCLP procedure [12].

In order to calculate general toxicity, the published data where concentrations of heavy and toxic metals were determined according to the TCLP procedure were applied [13, 14].

Results and discussion

The test of toxic leaching assumes that wastes are submitted to react with more aggressive leaching agents than with those which can occur in natural soil environment [15, 16]. The limit of toxic leaching procedure for each metal leached from soil or sludge was established at the level of hundred times exceeding the maximum concentration of metal pollutions in potable water. For instance, for cadmium: 0.01 mg/dm^3 in potable water, and 1.0 mg/dm^3 - a limit value of toxic leaching [17]. Eluted or toxic forms of metals, eg, lead, make as a rule approx. 10÷30% of total value of metal data determined in concrete environmental components or in wastes [18, 19]. With this respect, it was not possible to use data of metals total concentrations to undertake modelling attempts. The selection of gradient factors for polynomial equation was based on permissible limit values for metals in TCLP procedure, presented in Table 1.

Table 1

Limit, permissible contents of toxic metals according to the TCLP criterion [12, 20]

Toxic metals	Pb	As	Ba	Cd	Cr	Hg	Se	Ag
Maximum concentration of toxic metals acc. to TCLP [mg/dm^3]	5	5	100	1	5	0.2	1	5

Gradient factors were selected by using weighted mean method, considering a number of metals with toxic concentrations basing on the criteria stated in TCLP procedures for the assessment of general toxicity of the indicated waste. On the ground of the achieved results an attempt was made to indicate which of the tested wastes should be classified as wastes toxic for the environment and which ones can be treated as environmentally safe. The

assessment of the toxicity level (y) for the indicated group of wastes was quantified with the assumption of the following criterion:

$y(x_1, x_2, x_3, \ldots, x_n) \geq 1$ - the tested waste is environmentally toxic;

$y(x_1, x_2, x_3, \ldots, x_n) < 1$ - the waste is not toxic.

It was assumed that the contents of forms of the leached metals with toxic concentrations in wastes is hazardous for the components of ecosystems when the value of general toxicity fulfils the following relationship $y(x_1, x_2, x_3, \ldots, x_n) \geq 1$. For instance, in order to make computations, concentrations of toxic metals [mg/dm^3] determined in samples of processing wastes (A1-A3) and hospital wastes (B1 and B2) were used acc. to TCLP procedure, and the experimental data for one's own calculations were taken from reports [13] and [14] (Table 2).

Table 2

The level of metal concentrations [mg/dm^3] in exemplary processing wastes A(1-3) and hospital wastes B(1, 2) determined acc. to the TCLP procedure and used for one's own modelling attempts

Metal / Sample	As	Ba	Pb	Ag	Cd	Cr
A1[a)]	3.5	-	16	-	1.26	32
A2[a)]	9.1	-	15	-	1.28	31.2
A3[a)]	6.3	-	18.3	-	1.12	30.4
B1[b)]	41.01	38.67	16.75	6.59	-	20.64
B2[b)]	28.2	46.96	7.93	3.86	-	36.82

where: the experimental data were taken from reports: [a)] [13], [b)] [14]; gradient factors were matched basing on literature data, respectively, for: As - 0.31 [13] and 0.0417 [14], Cd - 0.06 [13], Cr - 0.31 [13] and 0.0417 [14], Pb - 0.31 [13] and 0.0417 [14], Ba - 0.8333 [14], Ag - 0.0417 [14]

Basing on the experimental data found in literature, the assumed model of general toxicity was computed and the results were listed for the analyzed types of wastes in Table 3.

Table 3

A list of calculated general toxicity values (y) according to the assumed model

$y(x_1, x_2, x_3, \ldots, x_n) = ax_1 + bx_2 + cx_3 + \ldots + nx_n$

Sample	Calculated general toxicity value $y(x_1, x_2, x_3, \ldots, x_n)$	Assessment of waste in accordance with the assumed criterion	Verified values of general toxicity [c)]
A1[a)]	16.04	y > 1, the waste qualified as toxic	52.76
A2[a)]	17.22	y > 1, the waste qualified as toxic	56.58
A3[a)]	17.12	y > 1, the waste qualified as toxic	56.12
B1[b)]	36.00	y > 1, the waste qualified as toxic	123.66
B2[b)]	42.30	y > 1, the waste qualified as toxic	123.77

where: calculations were based on the experimental data published in reports: [a)] [13], [b)] [14]; [c)] made on the TCLP criterion [12, 20]

Calculations of general toxicity and their verification, confirm the toxicity of two types of wastes exemplary selected for the needs of modeling.

Conclusion

The search for simple mathematical models to assess general toxicity of the tested wastes basing on the known contents of metals speciation fractions is an issue of current interest regarding mathematical modelling for the needs of the essential problems concerning environmental protection. The static predictive and polynomial model for the assessment of general toxicity of wastes could be applied for experimental data obtained in tests of sequential extraction, for instance, for the so-called ion-exchanging and carbonate fractions which are comparable with the values achieved using the TCLP procedure.

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PRÓBY MODELOWANIA MATEMATYCZNEGO NA POTRZEBY OGÓLNEJ OCENY TOKSYCZNOŚCI ODPADÓW ZAWIERAJĄCYCH METALE

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Abstrakt: Próby wstępnej oceny ogólnej toksyczności odpadów, zawierających w swoim składzie metale, w tym przede wszystkim ciężkie, wykonano za pomocą wielomianowego, statycznego i zarazem prognostycznego modelu matematycznego. Ogólną toksyczność wyznaczono dla próbek odpadów, w których metale były oznaczone metodą toksycznego ługowania TCLP (*Toxicity Characteristic Leaching Procedure*). Kierunkowe współczynniki (a, b, c, …, n) do równania ogólnej toksyczności postaci $y(x_1, x_2, x_3, \ldots, x_n) = ax_1 + bx_2 + cx_3 + \ldots + nx_n$ dobierano metodą średniej ważonej, biorąc pod uwagę zawartość poszczególnych metali oraz ich właściwości toksykologiczne. Poszukując kryterium oceny, przyjęto, że zawartość form wymywanych metali o stężeniach toksycznych w odpadach może być zagrożeniem dla komponentów biosfery wówczas, gdy wartość ogólnej toksyczności spełnia zależność $y(x_1, x_2, x_3, \ldots, x_n) \geq 1$. Bezwzględną wartość toksyczności ogólnej (y) wyznaczano, sumując oznaczone doświadczalnie poszczególne szczątkowe stężenia pierwiastków, zaznaczając ich udział ważony w ogólnej puli toksyczności. Na podstawie obliczeń dla przyjętego modelu ogólnej toksyczności wytypowanych odpadów i weryfikacji modelu względem kryteriów toksyczności zdefiniowanych w metodyce TCLP stwierdzono zbieżność uzyskanych wyników.

Słowa kluczowe: ocena ogólnej toksyczności, modelowanie matematyczne, metale o stężeniach toksycznych

Iwona RYKOWSKA[1] and Wiesław WASIAK[1]

BIOCONCENTRATION OF MERCURY AND HEAVY METALS BY THE BARK OF MAPLE-LEAF PLANE TREE

BIOKONCENTRACJA RTĘCI I METALI CIĘŻKICH PRZEZ KORĘ PLATANA KLONOLISTNEGO

Abstract: Continuous civilization progress, urbanization, and growing level of industrialization cause the fact that the contents of mercury and heavy metals in the natural environment is increasing, posing a threat to proper ontogenesis of all living organisms. Thus it is justified to monitor and control the accumulation of the above-mentioned elements in the environment. The main goal of our research was to determine whether maple-leaf plane tree (*Platanus x acerifolia*) may be used as a bioindicator of the air pollutants. This tree may be found all across Central Europe, it is quite resistant to different environment pollutions, and, what is very important, it sheds the bark every autumn. The research covered a determination of the analytical procedure capable of quantitive analysis of the contents of some given heavy metals: copper, zinc, iron, mercury and sulfur. The results and correctness of the procedure of the preparation of the bark samples for the analysis were confirmed by the research of a certified material (BCR-062 Olive leaves). Particular attention was put to the influence of the separated stages of the sample preparation (washing, drying, grinding down), especially for the mercury analysis due to the fact that this element is characterized by high volatility. To broaden the analysis, the samples were taken from different parts of the trees: limbs, trunks, and roots, as well as from different places, such as high-traffic streets, parks, and from different cities of Poland and Europe. Total mercury contents were measured by means of automatic Mercury Analyzer MA-2. The quantification determination of the transient-metal ions was performed on a emission spectrometer with inductively coupled plasma VARIAN VISTA-MPX.

Keywords: mercury, heavy metals, ICP-OES

Mercury, among other chemical elements, stands out from very high level of chemical and biological activity [1]. This element is very toxic, moreover, it is not subjected to biodegradation [2]. The toxicity of mercury is strongly correlated with its presence form, while the exposure depends on the way this element gets to the organisms. The emission of mercury to the atmosphere may be a result of some natural geochemical processes, biological methylation, as well human activities. Basic source of environmental-pollution mercury, being a result of human activities, is related with burning of the crude oil and coal, some smelting processes, battery and fluorescent-lamp production, and burning of waste materials [3-5]. Agriculture also participates in the pollution of nature environment by means of mercury - its derivatives are used for the production of seed grounds and some plant-protection preparations [1, 6]. For the non-industrial areas, elemental mercury dominates (98%) in comparison with mercury(II) in the aerosol and gaseous forms [7]. Small amount of mercury in the atmosphere is of organic nature, such as dimethylmercury and monomethyl mercury. Once emitted to the atmosphere as either bonded with some compounds, or as a vapour, mercury may be transported with the wind at a high distance. Mercury vapour is usually bonded by atmospheric dust, which in turn may be settled at the surface of the soil, water, and plants, polluting them. Mercury is quite easily absorbed by the plants (mainly the roots - 95%), also from the air.

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Recently, in European Union the emission of mercury considerably lowered; however, the concentration of this element in the environment still remains high. The report for the European Commission and Parliament in Brussels in the year 2005 pointed out an important issue for Poland as a leader in the liberation of mercury as a result of coal burning. Thus, it is appropriate to monitor and to control the accumulation of mercury in the natural environment in Poland and across Europe.

This work is devoted to the determination of total concentration of mercury and some heavy metals in the bark of the maple-leaf plane tree. For many years the bark of trees is a target for many researches on the elimination of pollution aspects related with heavy metals and organic compounds to be present in the air, in water solutions and sewage. As reported in the literature, so far the research was concentrated on such trees as: eucalyptus - *Eucalyptus camaldulensis* [8], guava - *Psydium guajawa* [9], pine tree [10], oak, fir tree, and spruce European tree [11, 12]. The main goal of the work was to determine whether maple-leaf plane tree (*Platanus x acerofolia*) may be used as an effective bio-indicator of the air pollution. This tree is to be found across almost all Middle Europe, is quite resistant to the pollution, and it throws down the bark every autumn and winter. Our research was concentrated on the determination of an analytical procedure capable of quantitive analysis of contents of such heavy metals, as copper, zinc, iron, manganese, mercury and, in addition, sulfur.

The results obtained as well as the accuracy of the proposed procedure of the preparation of the bark samples for the analysis was verified by the research on a certified material (BCR-062 Olive leaves). Particular attention was put on the influence of the stages of sample preparation (washing, drying, grinding, etc.), especially for such volatile element as mercury. In addition, the samples were (1) taken from different parts of a tree: branches, the trunk, and roots, (2) collected at different places (heavy-traffic streets, parks), and (3) in different cities and countries (Poland, Europe). Total concentration of mercury was determined by means of automatic mercury analyser Merkury Analyzer MA-2. The other above-mentioned heavy metals we determined by means of emission spectrometer with inductively-coupled plasma VISTA - MPX (VARIAN).

Reagents and methods

Sample preparation

- Sample collection

The samples of the bark of maple-leaf plane tree were collected from May to October 2008. The choice of the collection places was dictated by a differentiation of the places, from cities (Poland: Poznan, Kornik, Miedzyzdroje, Sopot, Europe: Vienna, Berlin, Padova, Rome, Slovakia - Tatrzanske Lomnice), to green areas such as parks. The samples were taken at the approximate height of 1 meter above the ground level.

- Preparation of the samples for the analysis

Samples of the bark were purified from the lichen by means of a ceramic knife. Next, the samples were cleaned by a tap water and further deionized water. Next, the bark was subjected to drying at the temperature 50°C, and grinded in an agate mortar. The grinded sample was drying till solid state at the temperature 110°C (approximately during 3 hours).

- Determination of total concentration of mercury

To determine total concentration of mercury, the method of cold vapur generation CV AAS was applied, by means of the automatic mercury analyzer MA-2. The determination procedure was composed of the following steps:

- Determination of concentration of metals (Cu, Fe, Mn, S, Zn)

Once the bark was prepared according to the above-described procedure, the samples were mineralized by means of the microwave mineralizer MDS-2000. The mineralization was performed inside Teflon bombs, in a mixture of 65% HNO_3 + H_2O_2 (5 : 2, 10 cm^3), at PSI 60 and POWER 40. After the mineralization the samples were put quantively to the 25 cm^3 flasks, supplemented by distilled water, and used for the determination of the above-mentioned heavy metals. The analysis was performed by means of the emission spectrometer with inductively coupled plasma ICP-MS of VARIAN company.

- Testing the quality of the determination method

To inspect the quality of the measurement, reference material BCR®-062 Olive leaves (*Olea europaea*) was applied. The determination of mercury concentration in the reference material was performed at the beginning and at the end of each experiment series. The certified concentration of mercury in the reference material was equal to 0.28 ± 0.02 mg · kg^{-1}. The measured (according to the above-described method) concentration was exactly 0.28 ± 0.01 mg · kg^{-1}. The certified concentration of copper in the reference material was equal to 46.6 ± 1.8 mg · kg^{-1}, manganese - 57.0 ± 2.4 mg · kg^{-1}, and zinc - 16.0 ± 0.7 mg · kg^{-1}, while the measured values for these metals 46.2 ± 0.5 mg · kg^{-1}, 56.8 ± 0.4 mg · kg^{-1}, and 15.8 ± 0.5 mg · kg^{-1}, respectively.

Results and discussion

The characteristics issue of the maple-leaf plane tree is related with shedding of the bark every year. Such a bark was inspected in our research, to determine the concentration of mercury and other elements, such as copper, iron, manganese, zinc and sulfur.

Table 1

Concentration of the metals under study [ppm] in the bark of maple-leaf plane tree, at some localization in Poland

Place	Concentration [ppm]					
	Hg	**Cu**	**Fe**	**Mn**	**Zn**	**S**
Miedzyzdroje 1	0.084 ± 0.010	4.1	84.5	12.1	9.0	700.7
Miedzyzdroje 2	0.062 ± 0.008	2.5	21.0	6.1	3.2	765.0
Sopot	0.065 ± 0.004	5.9	64.9	15.8	11.9	670.8
Kornik	0.14 ± 0.03	3.3	31.9	23.8	4.4	730.4
Poznan:						
PUE park 1*	0.063 ± 0.004	2.9	49.6	4.4	5.7	843.3
PUE park 2*	0.049 ± 0.005	2.1	31.4	4.4	2.2	592.2
Niepodleglosci Str. 1	0.13 ± 0.02	2.7	39.6	12.7	21.1	523.1
Niepodleglosci Str. 2	0.12 ± 0.02	1.7	12.2	4.5	7.5	494.1
Niepodleglosci Str. 3	0.14 ± 0.02	2.5	25.1	5.4	3.6	621.4
Niepodleglosci Str. 4	0.09 ± 0.04	8.6	156.9	19.9	17.6	584.8
Sniadeckich Str.	0.16 ± 0.03	10.0	222.9	19.1	24.4	1067.2

*Parks near Poznan University of Economics

The samples were taken from different parts of the tree: branches, trunk, and roots, as well as at different places across Poland and Europe. In Table 1 some results of determination of mercury and other heavy metals are given, for the samples collected in Poland, while in Table 2 - for the samples collected across Europe.

Table 2
Concentration of the metals under study [ppm] in the bark of maple-leaf plane tree, at some localization in Europe

Place	Concentration [ppm]					
	Hg	Cu	Fe	Mn	Zn	S
Berlin	0.063 ± 0.003	4.6	39.8	25.1	16.5	1016.6
Padova	0.086 ± 0.001	16.5	128.8	17.2	14.7	1075.5
Rome	0.067 ± 0.005	12.6	171.3	14.6	9.5	1345.3
Vienna	0.067 ± 0.004	9.0	80.8	24.7	21.8	920.6
Slovakia - Tatrzanske Lomnice	0.078 ± 0.006	4.5	46.0	201.7	52.0	485.9

As it may be deduced from an analysis of the results presented in Table 1, the concentration of the metals is different for different samples. This situation may be caused by the fact that the samples were collected from the places of different nature, such as the streets or the green areas (parks). The highest concentration of all the elements under study was detected at Sniadeckich Str. in Poznan. This place is located very close to the city center, moreover, Faculty of Chemistry and a big hospital are nearby. The lowest concentration was detected for a park near Poznan University of Economics (PUE) - this place is quite separated from the city traffic. Sample No. 4 was taken from a young tree at Niepodleglosci Str., Poznan. In this case large concentration was detected of such elements as copper, zinc and iron. These metals are responsible for proper ontogenesis, growth, and metabolism of the tree, as well as for photosynthesis process. High concentration levels are probably caused by intensive growth of this young tree. At the seaside, concentration levels of mercury are very similar (0.06÷0.08 ppm). Such low concentration is probably related with low emission to the atmosphere, and strong winds to and from the sea, forcing the replacement of the pollutants at a higher distance.

As it may be deduced from an analysis of the results presented in Table 1, the concentration of the metals is from 0.06 to 0.08 ppm. The highest concentration was detected in Padova (Italy) - this fact is probably related with a presence of large mercury deposits nearby. The concentration of manganese for the sample from Slovakia (Tatrzanske Lomnice) is pretty high - 201.7 ppm. It may be justified by the presence of large deposits of the ore of this element in this region, as well as related industry. Unfortunately, this area is poor in pyrite deposits, thus low concentration levels determined for sulfur and iron, in comparison with other European cities. On the contrary, Rome (Italy) area is reach in pyrite deposits, thus the concentration levels of sulfur and iron are high. In the bark collected in Berlin (Germany), lowest concentration levels were detected for such elements as mangan, iron, zinc and sulfur. Probably, the soil there was drain of its nutrients, these elements included. It proofs the fact that the concentration levels of the metals in the bark are related with the corresponding levels for the soil. Heavy metals are cumulated by the vascular plants, however, in a smaller amounts than the moss.

In Table 3 some results are given of the analysis of concentration of heavy metals in different parts of the maple-leaf plane tree (branches, trunk, roots). The samples were taken at Sniadeckich Str., Poznan, Poland.

Table 3

Concentration of the metals under study [ppm] in the parts of the plane tree

Maple-leaf plane tree	Concentration [ppm]					
	Hg	**Cu**	**Fe**	**Mn**	**Zn**	**S**
branches	0.26 ± 0.03	6.5	106.3	17.4	9.9	870.1
trunk	0.16 ± 0.03	10.0	222.9	19.1	24.4	1067.2
roots	0.21 ± 0.06	2.0	264.3	14.0	14.5	727.2

As it may be deduced, the highest concentration of the mercury was detected in the branches, while the lowest - in the trunk. It is probably caused by the fact that the adsorption of the pollutants by the bark is conditioned by wet and dry deposition, which in turn is conditioned by the size of the tree crown. Thus, the pollutants carried by the wind are mainly deposited at the branches and leaves. The high concentration of mercury in the roots may be explained by the fact that the pollutants are present in the soil, as a result of the contact with the rain water, and the city-polluted atmosphere.

Conclusions

While analyzing the bark of the maple-leaf plane tree, one may uncover important information about a level of degradation of the natural environment, from the moment of the development of the new bark, to its shedding. What is particularly important is the procedure of sample preparation, as improper treatment of the samples may significantly rise the detected concentration levels. By means of the proposed method, while undertaking the research on plant samples we are able to determine the contents of the pollutants not only at the plant surface, but also inside the plants.

To determine the pollution level one has to collect the samples from different, well-matched places, taking into account not only the localization of the place, but also tree part. One must note that some parts of the tree are subjected to decomposition, sometimes fast.

According to the samples we collected for this research, the highest concentration of the pollutants is usually determined for the crowded city streets, while the lowest - for the parks, even inside urban area.

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BIOKONCENTRACJA RTĘCI I METALI CIĘŻKICH PRZEZ KORĘ PLATANA KLONOLISTNEGO

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Abstrakt: Ciągły rozwój cywilizacyjny, urbanizacja, postępujące uprzemysłowienie sprawiają, iż zawartość rtęci i metali ciężkich w środowisku naturalnym wzrasta i stwarza zagrożenie dla prawidłowego rozwoju wszystkich organizmów. Wydaje się więc celowe, aby monitorować i kontrolować akumulowanie wspomnianych pierwiastków w naszym środowisku. Celem badań było określenie, czy platan klonolistny (*Platanus x acerifolia*) może służyć jako bioindykator zanieczyszczeń powietrza. Drzewo to występuje prawie w całej Europie Środkowej, jest stosunkowo odporne na zanieczyszczenia środowiska, a jego cechą charakterystyczną jest zrzucanie kory. Przeprowadzone badania obejmowały opracowanie procedury analitycznej pozwalającej na analizę ilościową zawartości wytypowanych metali ciężkich: miedzi, cynku, żelaza, manganu, rtęci oraz dodatkowo siarki. Wyniki i poprawność stosowanej procedury przygotowania próbek kory do analizy potwierdzono badaniami materiału certyfikowanego (BCR-062 Olive leaves). Zwrócono szczególną uwagę na wpływ poszczególnych etapów przygotowania próbek (mycie, suszenie, rozdrabnianie itd.), co zwłaszcza w przypadku rtęci ma bardzo duże znaczenie z uwagi na jej dużą lotność. Ponadto przebadano próbki pochodzące z różnych części drzewa: konary, pień i korzenie. Kolejną zmienną były miejsca pobrania próbek, kora drzew rosnących przy ruchliwych ulicach, w parkach, pobrane w różnych miastach Polski i Europy. Całkowitą zawartość rtęci oznaczono, wykorzystując automatyczny analizator rtęci Merkury Analyzer MA-2. Pozostałe metale ciężkie oznaczono na spektrometrze emisyjnym z indukcyjnie sprzężoną plazmą VISTA - MPX firmy VARIAN.

Słowa kluczowe: rtęć i metale ciężkie, ICP-OES

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EFFECT OF DIFFERENT LYMPHOCYTE-BACTERIA RATIOS AND BACTERIAL TOXINS ON APOPTOSIS OF BOVINE MAMMARY GLAND LYMPHOCYTES

WPŁYW STOSUNKU STĘŻEŃ LIMFOCYTÓW DO BAKTERII ORAZ TOKSYN BAKTERYJNYCH NA ŚMIERĆ LIMFOCYTÓW SUTKÓW JAŁÓWEK

Abstract: *Staphylococcus aureus* and *Streptococcus uberis* delay apoptosis of bovine mammary gland lymphocytes following intramammary infusion and in *in vitro* studies with lymphocyte-bacteria ratio 1:1. In this study, we investigated the effect of different lymphocyte-bacteria ratios on apoptosis of bovine mammary gland lymphocytes *in vitro*. We found out that lymphocyte-bacteria (*S. aureus* or *S. uberis*) ratios 1:10, 1:50 and 1:100 have different effect on apoptosis of lymphocytes than ratio 1:1. Lymphocyte apoptosis was induced 6 hours following incubation with *S. aureus* or *S. uberis* with mentioned ratios (1:10, 1:50 and 1:100). In our previous preliminary experiments focused on exploration of chemical components of bacteria on apoptosis of lymphocytes, we established the effect of muramyl dipeptide and lipopolysaccharide on lymphocyte apoptosis only *in vitro*. Therefore, in the second part of the present study we focused our experiments on investigation of the effect of Gram-negative bacterial toxin lipopolysaccharide on apoptosis of bovine mammary gland lymphocytes *in vivo*. The results of these experiments suggest that lipopolysaccharide induces apoptosis of lymphocytes following intramammary application. These data need next exploration to reveal detail effects of bacteria or bacterial toxins on lymphocyte programmed cell death in connection with inflammatory process.

Keywords: bacteria, bacterial toxin, apoptosis, lymphocyte, mammary gland

Bacterial pathogens modulate apoptosis of cells [1]. Pathogens which are involved in the cell death of lymphocytes include Gram-positive or Gram-negative bacteria [1-3] and their components, especially bacterial toxins such as *lipopolysaccharide* (LPS) [4-6]. *Staphylococcus aureus* and *Streptococcus uberis* are the most important pathogens causing clinical and subclinical bovine mastitis [7, 8]. Resident and incoming leukocytes play an important role in the mammary gland's defence system against invading pathogens. Macrophages and lymphocytes are the predominant resident cells in the healthy mammary gland, while intramammary infections induce the recruitment of leukocytes (and especially neutrophils) from blood into the mammary gland [9, 10]. During bouts of acute mastitis caused by staphylococcal or streptococcal infections, an increased number of lymphocytes are detected in the mammary glands [11].

Bacterial toxins and components are common constituents of environment entry to food chain. Thus they can be posing a risk for human population. Bovine strains of *S. aureus* associated with intramammary infection produce staphylococcal enterotoxins [12, 13]. Staphylococcal enterotoxins are known as superantigens [14]. The interactions of superantigens with the T cells lead to their activation [15] and apoptosis [16, 17]. Haslinger et al [18] reported that *S. aureus* α-toxin induced apoptosis in human peripheral blood

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mononuclear cells. Park et al [19] investigated apoptosis of $CD4^+$ and $CD8^+$ lymphocytes of bovine blood during *in vitro* cultivation with staphylococcal enterotoxin C, after previously demonstrating that staphylococcal infections induce immunosuppresive $CD8^+$ T cells *in vivo* [20, 21]. LPS is as a toxin released from the cell wall of Gram-negative bacteria. Infusion of LPS into the bovine mammary gland induces an inflammatory response [22-24].

In our previous study, we have demonstrated the effect of *S. aureus* and *S. uberis* on apoptosis of bovine mammary gland lymphocytes. We found out that apoptosis of lymphocyte was delayed during an experimentally induced infection with *S. aureus* or *S. uberis*. These results were confirmed by *in vitro* experiment with lymphocyte-bacteria ratio 1:1. Some authors described a possible role of different lymphocyte-bacteria ratio on apoptosis of lymphocytes such as Perticarari et al [25]. They focused their experiments on exploration of the effect of *Borrelia burgdorferi* on apoptosis of human lymphocytes *in vitro* with lymphocyte-bacteria ratios 1:10, 1:20, 1:50, 1:100.

The aim of our study was to determine the effect of different lymphocyte-bacteria ratios and *Escherichia coli* LPS on apoptosis of bovine mammary gland lymphocytes.

Materials and methods

The experiments were carried out on 16 mammary glands of 4 clinically healthy Holstein × Bohemian Red Pied crossbred heifers aged 16 to 18 months - *in vivo* experiments followed *in vitro* experiments in the same animals. The heifers were housed in an experimental tie-stall barn and fed a standard ration consisting of hay and concentrates with mineral supplements. The experimental tie-stall used in this study is certified and animal care conformed to good care practice protocols. All heifers were free of intramammary infections, as demonstrated through a bacteriological examination of mammary lavages.

The heifers were used as mammary gland cell donors for *in vitro* studies. Lymphocytes from the mammary glands were harvested following the *phosphate buffered saline* (PBS) intramammary injection, using a procedure previously described by Rysanek et al [26] that employs a model of an induced influx [27]. Fresh mammary gland leukocytes were adjusted (1.0×10^7 cells/cm^3) in RPMI 1640 medium (Sigma, MO, USA), both with and without *S. aureus* and *S. uberis*, at a ratio of 1:1, 1:10, 1:50 and 1:100. The two bacterial strains used were *S. aureus* Newbould 305 (CCM 6275) and *S. uberis* (CCM 4617). The samples were incubated at 37°C in a 5% CO_2 atmosphere for 1, 3 and 6 hours, as described by Scaife et al [28]. After incubation, apoptotic lymphocytes were detected through *flow cytometry* (FCM) (FACS Calibur apparatus, Becton Dickinson, CA, USA).

Before experimental infection, the mammary glands were treated with PBS prepared with apyrogenic water. All 4 mammary gland sinuses of each heifer were rinsed stepwise with PBS to obtain a cell suspension using the following procedure. The first cell sample was obtained by lavage of the left forequarter 1 day after administration of PBS. The remaining quarters were rinsed stepwise at two 1-day intervals and one 4-days interval in the following order: left-rear (2 days) → right-front (3 days) → right-rear (at 7 days). These PBS-treated mammary glands were set as a control for the infections, as undertaken in previous studies [29, 30]. LPS of *E. coli*, serotype 0128:B12 (Sigma, USA) in a concentration of 5 µg in 20 cm^3 PBS was used for inducing inflammatory response. Modified urethral catheters (AC5306CH06, Porges S.A., France) were inserted into the teat

canal following thorough disinfection of the teat orifice with 70% ethanol. Through the catheter, each mammary quarter was injected with 20 cm^3 of PBS and 2 cm^3 of lavage solution was immediately collected back through the catheter directly to the syringe and subsequently used for bacteriological examination.

Apoptotic lymphocytes were analysed by FCM following simultaneous staining with Annexin-V labelled with *fluorescein isothiocyanate* (FITC) and propidium iodide, as described by Vermes et al [31]. The commercial Annexin-V-FLUOS staining kit (Boehringer Mannheim, GmbH, Mannheim, Germany) was used according to the manufacturer's instructions. Briefly, 500 mm^3 of the incubation buffer (10 mM Hepes/NaOH, pH 7.4; 140 mM NaCl; 2.5 mM $CaCl_2$) was mixed with 10 mm^3 of PI and 10 mm^3 of FITC-Annexin-V solution. After 15 min of incubation at room temperature with fresh buffer containing PI and FITC-Annexin-V, the cell suspension was analysed by FCM with differentiation of at least 20,000 cells. After labelling with Annexin-V-FITC and PI, lymphocyte cells were distributed over three different quadrants of a dot plot analysis (with FL1 and FL3 axes), representing viable (Annexin V^-/ PI^-), apoptotic (Annexin V^+/PI^-), and necrotic cells (Annexin V^+/PI^+). Dot plots were evaluated qualitatively and quantitatively using WinMDI^{TM} software.

Arithmetic means and standard deviations were used to describe the apoptotic lymphocytes. Statistically significant differences in the proportions of apoptotic lymphocytes were determined using the paired *t*-test. The data were processed using Statistica 8.0 software (StatSoft CR Ltd, Prague, Czech Republic).

Results and discussion

The objective of this study was to determine the effect of different lymphocyte-bacteria (*S. aureus* and *S. uberis*) ratios on apoptosis of bovine mammary gland lymphocytes *in vitro*. In our previous study, we described that a significantly lower percentage of apoptotic lymphocytes were observed following cultivation of cells with *S. aureus* and *S. uberis* than following cultivation without bacteria (initial ration of lymphocyte to bacteria 1:1) [3]. In this study, we investigated an effect of different lymphocyte-bacteria ratios on apoptosis of lymphocytes. We found out that apoptosis of lymphocytes is significantly increased following 6 hours of cultivation with lymphocyte-bacteria ratios 1:10, 1:50 and 1:100, contrary to the ratio 1:1 (Figs 1 and 2). These results correspond with other experimental work focused on lymphocyte apoptosis co-cultured with *B. burgdorferi* [25]. The authors of that article showed that increasing lymphocyte apoptosis corresponds with increasing ratio (1:10 → 1:100).

The aim of this study was also to determine whether apoptosis of bovine mammary gland lymphocytes is modulated during an inflammatory response of bovine mammary gland induced by LPS of *E. coli*. Lymphocytes were obtained by lavage of the mammary gland at 4 intervals (1, 2, 3 and 7 days) following stimulation with LPS. Stimulation of mammary gland with LPS resulted in a significant increase in proportion of apoptotic lymphocytes in comparison with the control. The portion of apoptotic lymphocytes peaked at 2 days following stimulation. In previous studies, there was demonstrated that apoptosis of bovine mammary gland lymphocytes is delayed during an experimentally induced infection of bovine mammary gland with *S. aureus* and *S. uberis* and during an *in vitro*

cultivation with LPS and MDP [3, 6, 32]. However, results of this part of the study suggest that LPS intramammary application induces apoptosis of lymphocytes.

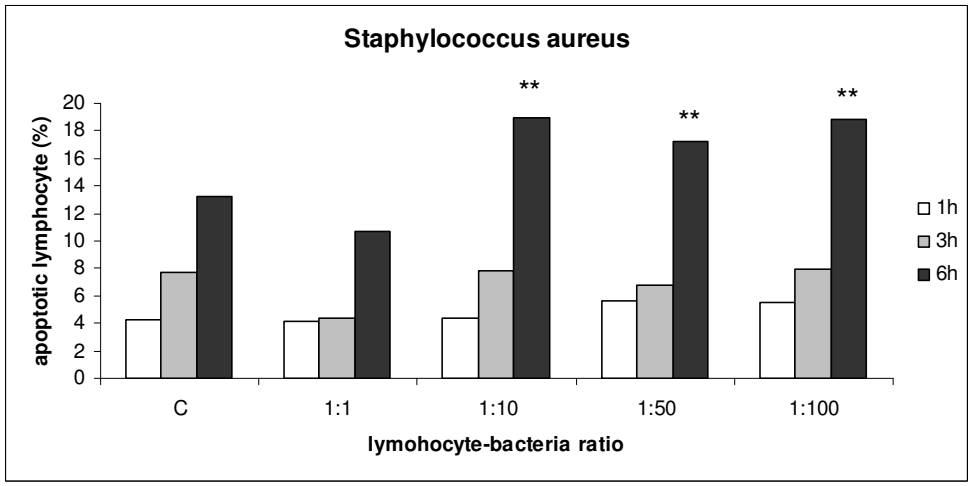

Fig. 1. The proportion of apoptotic lymphocytes in *in vitro* experiment with lymphocyte-bacteria (*S. aureus*) ratios 1:1, 1:10, 1:50, 1:100. C - control (cells only). Significant differences among the lymphocyte-bacteria ratio 1:1 and lymphocyte-bacteria ratios 1:10, 1:50, 1:100 are marked with asterisks (**p < 0.01)

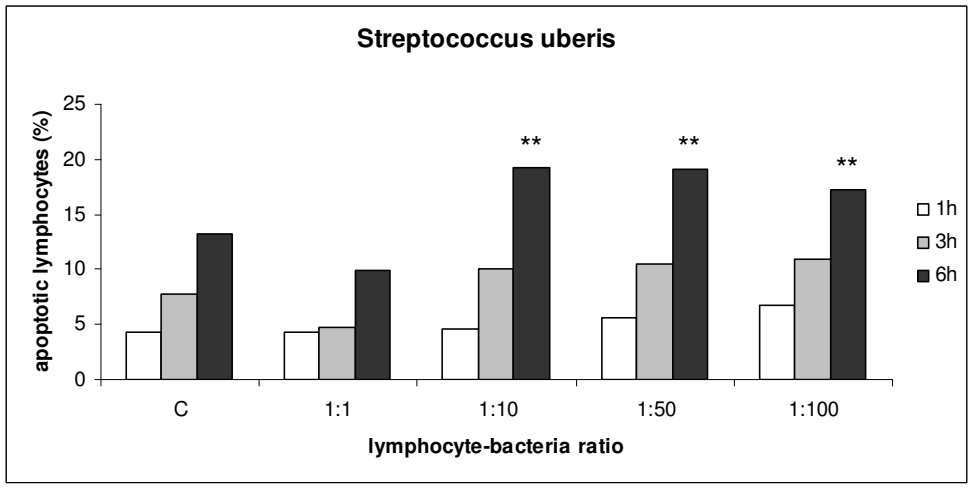

Fig. 2. The proportion of apoptotic lymphocytes in *in vitro* experiment with lymphocyte-bacteria (*S. uberis*) ratios 1:1, 1:10, 1:50, 1:100. C - control (cells only). Significant differences among the lymphocyte-bacteria ratio 1:1 and lymphocyte-bacteria ratios 1:10, 1:50, 1:100 are marked with asterisks (**p < 0.01)

Conclusions

The effect of bacterial pathogens on apoptosis of lymphocytes is depended on cell-bacteria ratio. Apoptosis of lymphocytes is induced in lymphocyte-bacteria ratios 1:10, 1:50 and 1:100, contrary to the ratio 1:1 which is connected with delaying of lymphocyte apoptosis.

Stimulation of bovine mammary gland lymphocytes *in vivo* with *E. coli* LPS leads to increase in apoptotic lymphocytes at variance with previous *in vitro* experiment with *E. coli* LPS that showed delaying of lymphocyte apoptosis.

To confirm these data, there is necessary next exploration to reveal detail effects of bacteria or bacterial toxins on lymphocyte programmed cell death in connection with inflammatory process.

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EXAMINATION OF CAPILLARY RISE PHENOMENON IN AERATED CONCRETE BLOCK USING THE SURFACE TDR PROBE

BADANIE ZJAWISKA PODCIĄGANIA KAPILARNEGO W BLOCZKU Z BETONU KOMÓRKOWEGO Z ZASTOSOWANIEM POWIERZCHNIOWEJ SONDY TDR

Abstract: Aerated concrete is the basic building material applied in traditional building industry. It is mainly caused by its thermal parameters - heat conductivity coefficient λ for lighter brands of this material is many times lower than other traditional materials like brick etc. Low value of heat conductivity coefficient is mainly caused by the material structure which is highly porous. This porosity causes capillary forces which are the reason of so called capillary rise phenomenon being the reason of many buildings destruction. This article presents the possibility of monitoring and quantitative valuation of moisture increase in building barriers due to capillary rise with the application of the TDR surface probes enabling quick and noninvasive moisture determination in porous building materials. The analyses conducted using surface TDR probes will be compared with the examinations made using other electrical methods and the results will be presented in the form of moisture profiles changing in time.

Keywords: capillary rise, aerated concrete, surface probes TDR

Aerated concrete is the one of the most popular building materials in the Polish market [1]. It is the artificial material with specific cellular structure which was intentionally designed to obtain suitable bearing and thermal parameters. The structure of aerated concrete consists of the air gaps called pores which can differ in volume and shape within a single sample of the material [2].

With its porous structure the aerated concrete is a very good building material. Especially its thermal properties make it a particularly interesting option from the point of view of ecology and Environmental Engineering. Many literature sources [3-5] and normatives (PN-EN ISO 6946) inform that the value of thermal conductivity λ of aerated concrete varies between 0.1 and 0.25 W/mK depending on apparent density and moisture which makes it even 10 times better than the other materials like red ceramic brick or stones.

It should be also underlined that many of its production technologies utilize ashes from power plants [6] which satisfies the idea of Sustainable Building [7] in two most important fields:

- building materials production,
- building exploitation.

On the other hand, this complicated porous structure of aerated concrete strongly influences its water parameters because the empty pores attract water molecules to fill the air gaps. This phenomenon called capillary rise is a serious reason of many objects

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destruction. Porous building materials like aerated concrete absorb water from the ground, waterfalls, floodwater or sanitary installations fails in the common phenomenon called capillary rise.

All above-mentioned parameters and problems connected with the aerated concrete are the reason to develop a handy method of water presence detection which could enable quantitative moisture determination in building barriers. Determination of moisture and its changes monitoring in particular periods may enable easier finding of the problem source and may give the indications how to remove the problem.

Traditionally used direct, gravimetric methods, despite their accuracy are not perspective in this branch because they are invasive, require sampling and, what is perhaps the biggest problem, are significantly time-consuming. That is why, especially for monitoring and *in-situ* measurements, they are successfully being replaced by the indirect methods which offer less accuracy, but otherwise provide quick results and in some cases give the possibility of constant monitoring of moisture changes phenomena.

Among the indirect methods two electric ones are presented in this paper. They measure one of the the electric parameters of the material which is dependent on water content - dielectric permittivity. Dielectric permittivity of the moist material can be measured in *Frequency Domain* (FD) and *Time Domain* (TD) methods. FD method [8] is a capacitance method, which relies on the determination of condenser capacity. This method enables quick moisture determination with simple, user friendly mobile devices - Figure 1a which are noninvasive and do not require samples preparations. Among the Time Domain methods the most popular is the TDR method, which was successfully used for moisture determination of the soils [9-11] and building materials [12-17]. Until now, application of the TDR method with building materials was problematic due to the necessity of probes internal installation which was only possible to apply in laboratory conditions and rather for soft building materials [18, 19].

Since several years the surface TDR probe is developed which seems to be perspective for noninvasive moisture determination in building materials. The idea and parameters of the presented surface TDR probe are presented in the following papers [20-23]. Figure 1b presents the example of the surface TDR probe manufactured at Lublin University of Technology.

a) b)

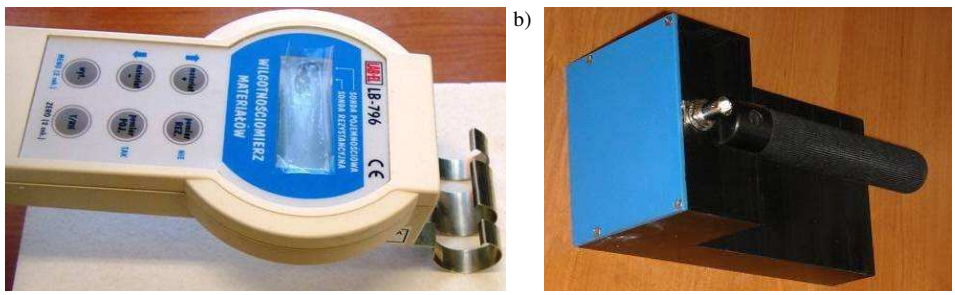

Fig. 1. Probes applied in described experiment: a) capacitance moisture probe, b) surface TDR probe

In this article we present the possibility of monitoring of capillary rise phenomenon using the capacitance and surface TDR probes in blocks of aerated concrete.

Materials and methods

The experimental setup consisted of:

- TDR surface probe presented in Figure 1,
- TDR Soil Multimeter (Easy Test),
- PC computer controlling the TDR device,
- LB-796 capacitance moisture meter (Label, Figure 1),
- aerated concrete sample (SOLBET Lubartow).

As a sample we used the block of aerated concrete produced by the local manufacturer SOLBET Lubartow. The sample dimensions were the following: 240×240×240 mm and its density in dry was about 700 kg/m^3. First the sample was dried in 105°C and put into the water container. The bottom of the sample was one centimeter under water level which was kept constant by the specially prepared device. The reference points were signed every 5 centimetres above water level and during the experiment they shown the measuring points (5, 10, 15 and 20 cm).

The measurements were conducted manually in period of 16 days with the irregular time steps (in most cases three measuring series per day).

Results

The experimental results are presented in Figures 2 and 3 in the form of the process diagrams at the particular heights. The diagram 2 presents readouts obtained with capacitance probe and Figure 3 shows the readouts obtained with TDR device. Water content increase at each altitude is expressed by increased value at the ordinate axis.

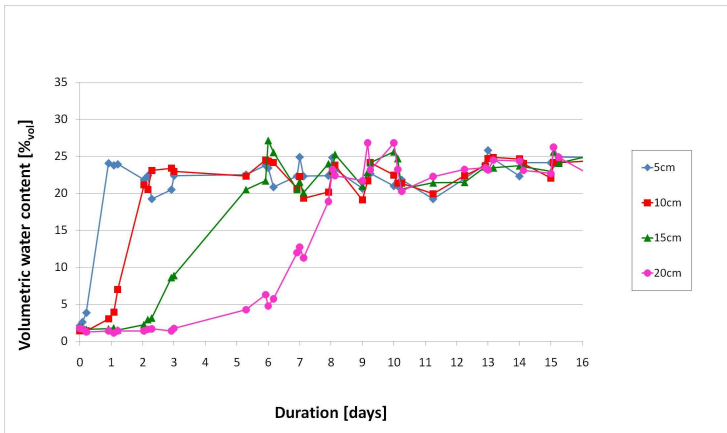

Fig. 2. Moisture changes in aerated concrete determined using capacitance method

The experiment confirms the phenomenon of capillary rise in aerated concrete and enables quantitative determination of its progress. In both diagrams the initial value of moisture is equal 0 which is the result of drying during sample preparations. Both probes show quick moisture increase at 5 cm reference point, the slope of the increase is very steep which proves high capillary forces of the material. After one day of the experiment it

reaches the maximum water content value. At higher altitudes moisture increase is shifted in time but also very quick. At 10 cm the first water presence is noticed after one day of the experiment but from that moment it increases quickly and after the next day it reaches the maximal value possible for this material. The rate of water content increase at 15 cm is slower than before. The first readouts are observed after 3 days of the process and the maximal value is noticed about 4 days later. Fourth, the highest reference point, placed at the height of 20 cm shows water presence after the period of 6 days and then it gently rises to reach high values after the next 4 days but its maximum value was noticed at the end of the whole presented experiment.

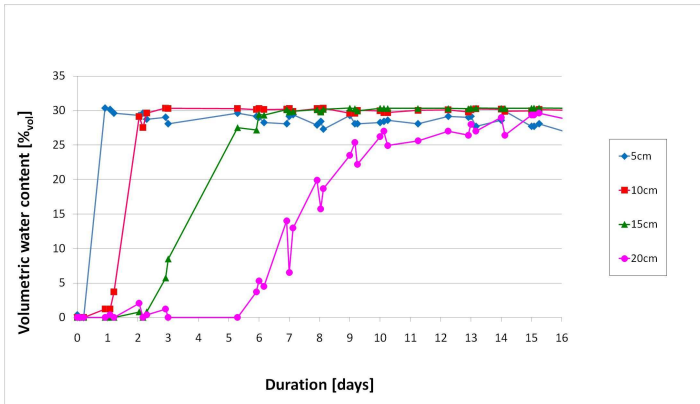

Fig. 3. Moisture changes in aerated concrete sample determined using surface TDR probe

Both experiments show very similar process progress. The major noticed differences are the following:

- Maximum water content read by the capacitance probe was less than TDR surface probe.
- In high water states moisture readouts by the capacitance probe were less stable than TDR readouts.
- In low water content and intermediate states the process readouts determined with capacitance and TDR probe were comparable.

Conclusions

- The experiment confirms the potential of TDR technique for moisture processes monitoring in building materials. Application of the surface TDR probes enables quantitative determination of moisture changes in the material profile without the necessity of invasive probes installation which may be successfully used in *in situ* experiments.
- Comparing with the traditional invasive TDR experiments of capillary rise, surface TDR probes show greater results dispersion which is compensated by the simplicity of application and no drilling is required.
- The reasons of this increased dispersion are the smaller resolution of surface probes and the increased influence of other factors connected with permanent probe

repositioning. In case of traditional TDR measurements the probes are buried inside the material. In the described experiment the probes position was permanently moved from one to other reference point which could increase the readouts dispersion.

- Capacitance probe readouts showed underestimated values of maximum water content. Also the readouts dispersion was greater than in presented TDR measurements. This can be explained by the salinity influence on capacitance measurement - especially in high water content states.

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BADANIE ZJAWISKA PODCIĄGANIA KAPILARNEGO W BLOCZKU Z BETONU KOMÓRKOWEGO Z ZASTOSOWANIEM POWIERZCHNIOWEJ SONDY TDR

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Abstrakt: Beton komórkowy jest podstawowym materiałem budowlanym stosowanym w budownictwie tradycyjnym. Wynika to głównie z jego właściwości termoizolacyjnych - współczynnik przewodzenia ciepła λ dla lżejszych jego odmian jest wielokrotnie niższy od wartości tego współczynnika takich materiałów, jak cegła itp. Niska wartość współczynnika przewodzenia ciepła wynika głównie ze struktury materiału, która charakteryzuje się dużą porowatością. Z właściwością tą wiąże się fakt występowania sił kapilarnych, które są przyczyną zjawiska podciągania kapilarnego będącego przyczyną destrukcji wielu budynków dotkniętych nadmiernym zawilgoceniem. Artykuł przedstawia możliwość monitoringu i ilościowej oceny wzrostu wilgotności w przegrodach budowlanych wskutek procesu podciągania kapilarnego przy wykorzystaniu powierzchniowych sond TDR umożliwiających szybkie i bezinwazyjne wyznaczanie wilgoci w porowatych materiałach budowlanych. Analizy wykonane za pomocą sond powierzchniowych porównano z wynikami z innych metod elektrycznych i przedstawiono w postaci profili wilgotnościowych zmieniających się w czasie.

Słowa kluczowe: podciąganie kapilarne, beton komórkowy, powierzchniowe sondy TDR

Zbigniew SUCHORAB[1] and Marcin WIDOMSKI[1]

DETERMINATION OF SALINITY CHANGES IN BUILDING MATERIALS USING ELECTRIC METHODS

POMIARY ZMIAN ZASOLENIA W MATERIAŁACH BUDOWLANYCH ZA POMOCĄ METOD ELEKTRYCZNYCH

Abstract: Building materials salinity is an important exploitation problem of many objects, especially those which are built without obeying the essential rules connected with performing of waterproof insulation. Porous structure of building materials which form the building barriers is the cause of water capillary rise and thus the movement of salt ions which are the reason extensive barriers destruction. In high concentrations the salt ions crystallize inside the pores of building materials and are the reason of their destruction. It is especially visible in the form of dropping external layers from the walls - plasters, which are mainly vulnerable on the salinity phenomenon. Simulations and measurements of salinity change processes in building materials give the possibility to evaluate the threat and may help to choose the suitable renovation method. The paper presents measurements of water desorption in aerated concrete sample and also the simultaneous process of salinity change in particular layers of the material. The measurements of the above mentioned processes are done using TDR probes (*Time Domain Reflectometry*) which enable constant monitoring of water flow and thus salinity changes.

Keywords: salinity, monitoring, resistance, capillary rise

Many building objects both historical and currently built suffer the problem of excessive moisture which is mainly caused by their porous structure [1, 2] and the strong capillary parameters. In 2010 year the problem of water presence in building barriers became even more important because of the strong inundations which were noticed in the very extensive range of Poland and Central Europe. The problem which is directly connected with water presence inside the building materials structure is salinity. This is caused by the fact, that water is a great salts solvent which are often capillary risen from the soil or from the rain waters (acid rains). Salinity is the problem which leads to the building material structure and particularly to the external plasters demolition. This is mainly caused by the gradual ions concentration which leads to the internal crystallization and then material destruction. As it was mentioned before the problem is the most important in external layers, where the rate of water evaporation is the highest and the crystallization phenomenon the biggest. These salt crystals increase their volume and may destroy the air gaps and then decrease material's strength and insulation parameters.

In case of many old buildings it is even visible several years after the renovation processes, where the destruction and plasters demolition occurs. Salinity presence can be also noticed in the form of splashes in the external parts of red brick masonries.

The problem of extensive salinity presence in building barriers and materials is presented in the following papers [3-5].

All above mentioned problems are the reason to run investigations which may help to detect and predict the water and salinity presence in building barriers and materials. Methods which may be used for the above-mentioned tasks are the modeling and monitoring.

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This paper it is an attempt to model and quantitatively determine the process of moisture changes in a sample of aerated concrete. Aerated concrete was applied for our investigations because it is one of the most popular building material in Polish market [6]. Its structure is representative for any porous building material. Other interesting parameters of this materials have been presented in the following literature items: [2, 7].

In this paper we present the possibility of monitoring of water desorption and salinity changes in the sample of aerated concrete using the standard TDR (*Time Domain Reflactometry*) equipment.

Materials and methods

The experimental setup used for experiment consisted of the following elements:

- TDR Soil Multimeter (Easy Test),
- LP/mts TDR probes (Easy Test)
- PC computer controlling the TDR device,
- aerated concrete sample (SOLBET Lubartow), bulk density 700 kg/m^3.

As a sample we used the block of aerated concrete produced by the local manufacturer SOLBET Lubartow. The sample dimensions were the following: 60×240×240 mm. The sample was initially poured into the 0.5% mass solution of KCl (*Potassium Chloride*). After 5 days of moisturizing the obtained volumetric water content was about 27% vol. (maximum water content is estimated for 30% vol.) what was the initial value for the desorption experiment. Then the sample was covered with the bitumen layer to isolate it from the external environment parameters. Only the upper surface remained not isolated. In such a prepared sample a set of TDR probes was installed. For the experiment we used LP/mts probes by EasyTest, Lublin. LP/mts (*Laboratory Probes for moisture, temperature and salinity*) enable constant monitoring of moisture and salinity. Moisture determination was done using the TDR method (the determined parameter was time of signal propagation along the sensors [ps] and thus dielectric permittivity and moisture). To determine water content of aerated concrete the following calibration formula was used, previously developed by the authors of this article [8]:

$$\theta_{700} = -7.0 \cdot 10^{-4}\varepsilon^2 + 3.29 \cdot 10^{-2}\varepsilon - 1.05 \cdot 10^{-2}$$

where: θ_{700} - volumetric water of aerated concrete with bulk density 700 kg/m^3, ε - dielectric permittivity read by the TDR device.

Salinity was determined with electrical conductivity sensors which are built in the applied TDR probes and after the suitable calibration can determine saline ions concentration.

Calibration was conducted for each of four applied probes with the following KCl solutions: 0.5, 0.3, 0.1% and distilled water.

The TDR probes were invasively installed inside the structure of the material with the distance of 5 cm between each probe. The position of the first probe was 5 cm below the upper surface of the probe. The scheme of the experiment presents Figure 1. The experiment was conducted in isothermal conditions - 23°C (±0.5°C) during the period of 30 days (650 hours).

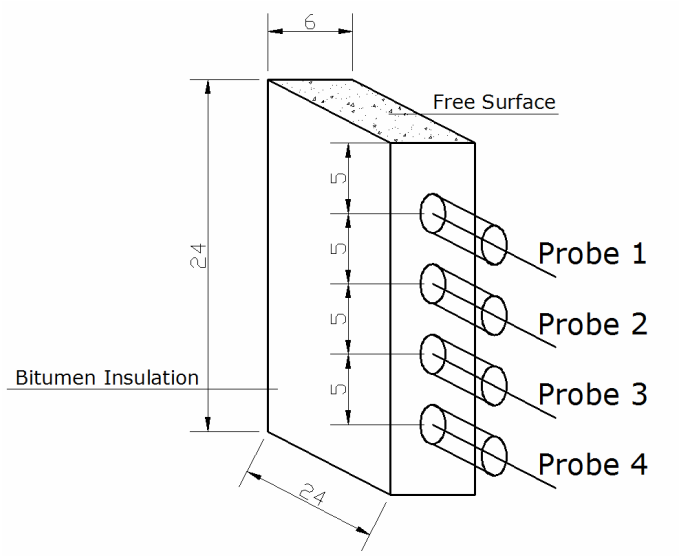

Fig. 1. Experiment setup

Results

With the calibration of the LP/mts for salinity determination the following formulas were obtained:

Table 1

Calibration formulas for salinity determination

Probe No.	Formula
1	$S = 5E^{-09}U^2 - 3E^{-06}U + 0.0018$
2	$S = 6E^{-09}U^2 - 2E^{-05}U + 0.0195$
3	$S = 5E^{-09}U^2 - 6E^{-06}U + 0.0063$
4	$S = 1E^{-09}U^2 + 3E^{-05}U - 0.0479$

where: S - salinity [% mass], U - voltage [mV].

The process of water desorption is presented in Figure 2.

From the diagram it is visible that during the period of 30 days water did not completely evaporated. The amount of water decreased for about 14% vol. - from the initial 26÷27% vol. to about 12% vol. The process progress indicates comparable desorption rate at each altitude. The differences can be recognized by some displacement of all 4 curves. Assuming that the method accuracy is about 0.5% vol. it is hard to predict if those displacements are caused by measurement errors or differences in process progress. The reason of such a situation may be the salinity ions presence which may reduce the TDR signal voltage and flatten the signal peaks from which the dielectric permittivity is determined. It will not influence the moisture readouts but may decrease the measurement accuracy.

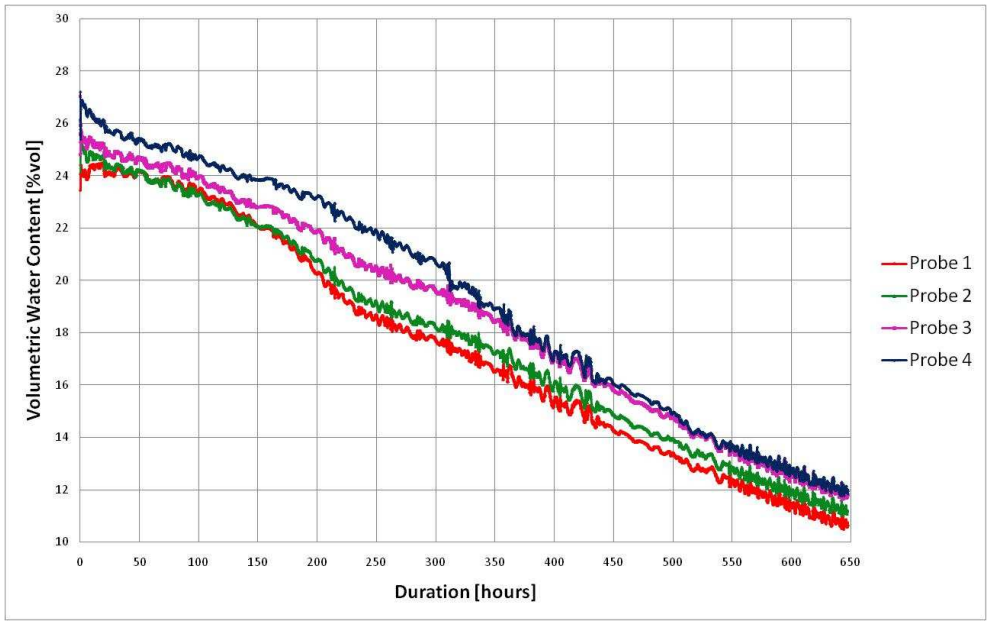

Fig. 2. Desorption process determined using TDR probes

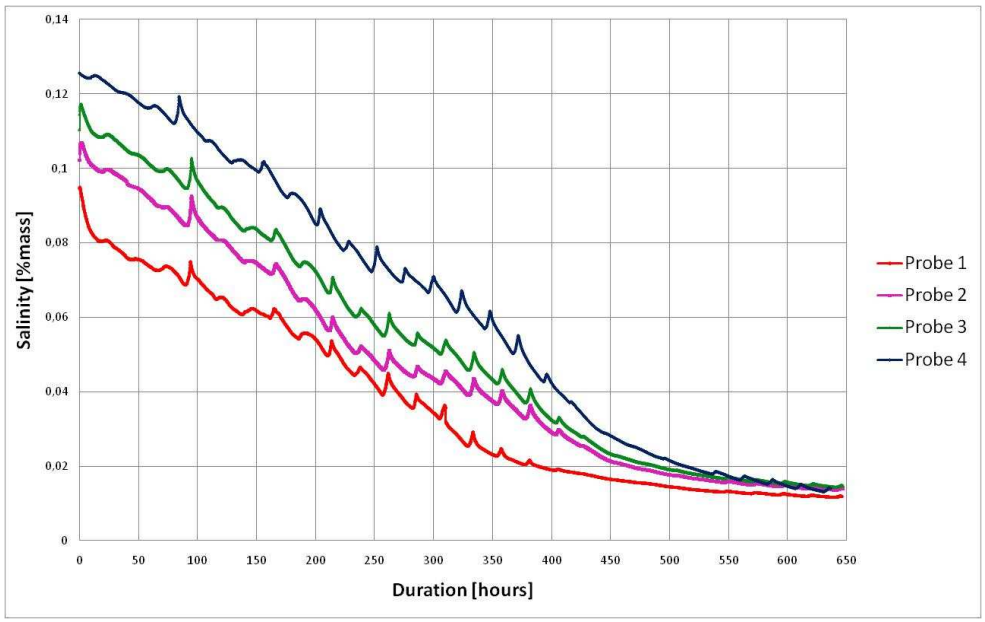

Fig. 3. Salinity changes in sample determined in described experiment

The results of salinity measurement are presented on Figure 3. The diagram below presents salinity change at each altitude of the sample. The curves symbolizing readouts on probes 1-4 start at the ordinate axis between 0.09 and 0.13% mass which can be interpreted as unequal location of salt ions inside the sample. The experiment indicates continuous decrease of salinity value on each probe to a final value 0.1% mass at the end of experiment at each probes.

Laboratory experiment confirmed that ions concentration within the material is combined with moisture. At low states of water content the salinity value is also very low (0.01%) and does not change with moisture changes anymore.

Conclusions

- Salinity presence may influence the measurement accuracy but does not influence moisture value read by the device. Application of moisture measurement method using capacitance or resistance probes would run to big measurement errors or even make it impossible to continue with the measurements.
- If volumetric water content of aerated concrete is below 10% vol. material salinity read by the described devices is close to zero.
- Time Domain Reflectometry (TDR) method enables constant quantitative monitoring of simultaneous processes of water and salinity flows.

Acknowledgement

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POMIARY ZMIAN ZASOLENIA W MATERIAŁACH BUDOWLANYCH ZA POMOCĄ METOD ELEKTRYCZNYCH

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Abstrakt: Zasolenie przegród budowlanych jest znaczącym problemem eksploatacyjnym wielu obiektów, w szczególności tych wzniesionych bez zachowania podstawowych zasad obowiązujących przy wykonywaniu zabezpieczeń przeciwwilgociowych i przeciwwodnych. Porowata struktura materiałów budowlanych, z których wzniesiono przegrody, sprzyja zjawisku podciągania kapilarnego wody, wraz z którą przenoszone są jony soli będące przyczyną przyspieszonego niszczenia przegród. W dużych stężeniach jony soli krystalizują wewnątrz porów materiałów budowlanych i są przyczyną ich niszczenia. Szczególnie jest to widoczne w postaci odpadających zewnętrznych powłok przegród budowlanych - tynków, które są najbardziej narażone na zjawisko zasolenia. Symulacje i pomiary przebiegu procesów zmian zasolenia przegród budowlanych dają możliwość oceny zagrożenia tym zjawiskiem i mogą być podstawą doboru właściwych zabiegów renowacyjnych. Artykuł przedstawia pomiary zjawiska desorpcji w modelowej próbce betonu komórkowego i następującą równolegle zmianę zasolenia w poszczególnych warstwach próbki wskutek powyższego zjawiska. Badania powyżej wymienionego procesu wykonano z wykorzystaniem sond TDR (*Time Domain Reflectometry*), które umożliwią jednoczesny monitoring zjawiska przepływu wody oraz zmian zasolenia.

Słowa kluczowe: zasolenie, monitoring, pomiary rezystancyjne, podciąganie kapilarne

Rafał WAWRZYNIAK[1] and Wiesław WASIAK[1]

MONITORING OF BIOGAS USED AS A SOURCE OF RENEWABLE ENERGY

MONITORING BIOGAZU JAKO ŹRÓDŁA ENERGII ODNAWIALNEJ

Abstract: Biogas is a mixture of many gasses to which the main contribution of two thirds is brought by methane (CH_4) and one third by carbon dioxide (CO_2), while the other components including steam occur in trace amounts. Effective control of the process of fermentation is based on controlling the following parameters: type and amount of the substrates supplied, temperature of the process, pH value, amount of short-chain fatty acids, the degree of filling of the fermentation tank and the chemical composition of the gas obtained. In this study the measurements of quantitative composition of biogas made by a popular portable biogas analyser GA2000 were verified by gas chromatography determinations. In the analyser the content of methane and carbon dioxide is made by a spectrophotometric method, while the content of oxygen and hydrogen sulphide is electrochemically measured.

Keywords: biogas, gas chromatography, biogas analyser, verification of measurements

Biogas is a product of a complex reaction known as methane fermentation. The organic substances are decomposed by bacteria into simple compounds, mainly methane and carbon dioxide. Besides these compounds, biogas contains many other components that are not inert in the conditions of installation needed for biogas production. Typical composition of biogas and description of their influence on biogas properties and biogas installation performance are given in Table 1.

Not each type of biogas can be used for energy production. The main criterion of biogas for such application is that it must contain at least 40% of methane. For the majority of substrates used, the content of methane is 60÷65% and the content of carbon dioxide is 35÷40%, however, some authors have reported the increase of carbon dioxide content in biogas up to 50÷60% [1]. As far as the contents of nitrogen and oxygen are concerned, these compounds occur at the ratio of 4:1 and get into the biogas produced at very low productiveness of source, eg at the waste dumping grounds, or during technological processes or they are added on purpose in the amount of 3÷5% [1] to ensure the correct course of biological desulphurisation.

Another important component is hydrogen sulphide (H_2S), whose content determines the biogas quality, although it occurs in trace amounts. Its content should not be too high as already in low concentrations it inhibits the process of decomposition and causes corrosion of the biogas production installation, including power-heat units and water boilers. Many producers of biogas generators admit the content of hydrogen sulphide at a level of 0.05% [2]. It should be also mentioned that a product of H_2S combustion is SO_2, so when biogas is subjected only to combustion in a flare the admitted concentration of H_2S is 0.1% [2]. Biogas also contains small amounts of carbon oxide, not exceeding 0.2%. The concentration of another biogas component ammonia is usually kept at a level below <0.1 mg m^{-3}. Its amount is closely related to the type of substrates used and in certain biogas samples the concentration of ammonia reached 150 mg m^{-3} [3]. Other impurities met

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in biogas include chlorine, fluorine and mercaptans, however, their concentration is below 0.1 mg m^{-3} and trace amounts of aromatic hydrocarbons: the concentrations of BTX are below 1 mg m^{-3} and the concentrations of PAH - below 0.01 µg m^{-3} [2]. Important is also the presence of siloxanes getting into the wastewater with cosmetic products, detergents or construction materials. They have deteriorating effect on biogas generators as their combustion in the presence of oxygen leads to formation of silica acting as abrasive material [4]. The above survey of the information on possible impurities of biogas and their effects illustrates the importance of monitoring of the chemical composition of the biogas produced.

Table 1

Typical components of biogas and their effect on biogas and biogas installation performance [2]

Component	Content	Effect
CO_2	25÷60%	- Lowers the calorific value - Causes corrosion if the gas is wet - Increases the methane number and the anti-knock properties of engines
H_2S	0÷0.5%	- Corrosive effect in equipment and piping system - Emits SO_2 on combustion
NH_3	0÷0.05%	- Emits NO_x on combustion - Increase the anti-knock properties of engines
Water vapour	1÷5%	- Causes corrosion of installation - Products of condensation can cause damage to the engine and choke installation
Dust	>5 µm	- Blocks nozzles and fuel cells
N_2	0÷5%	- Lowers the calorific value - Increase the anti-knock properties of engines
Siloxanes	0÷50 mg m^{-3}	- Act as abrasive material causing damage to the engine

Material and methods

Analysis of biogas components was made by a portable analyser GA2000 made by Geotech [5]. For determination of methane and carbon dioxide it uses a double beam of infrared radiation and a reference cell. Determination of oxygen, carbon oxide and hydrogen sulphide is made by electrochemical sensor. The device permits determination of methane to the content of 70%, carbon dioxide to 60%, oxide to 25%, carbon oxide and hydrogen sulphide to 500 ppm.

Fig. 1. Biogas analyser series GA2000

The accuracy of indications declared by the producer for CH_4 and CO_2 at their content above 15% is ±3% and for O_2 in the content up to 5% is ±1%. The accuracy of indications declared for H_2S and CO in the range up to 500 ppm is ±10%. According to the producer's recommendations the analyser was periodically subjected to calibration using a certified mixture containing 30% of methane, 20% of carbon dioxide and 100 ppm of hydrogen sulphide. The calibration for oxygen was performed with reference to its content in the air.

The intake of the biogas sample was continued until getting stabilised indications of the instrument.

The results presented in this paper were made to verify the indications of the above analyser by comparison with those obtained by gas chromatography. The biogas samples for analysis were placed in special bags made of Tedlar® designed for collection of gas samples, produced by SKC, of 1 dm^3 in capacity (Fig. 2) [6].

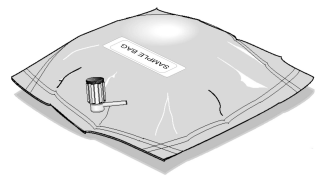

Fig. 2. A bag for collection of gas samples, the version with one valve

Each bag was filled with biogas with the help of a specially constructed kit enabling careful washing of the bag with the sample. Following the recommendations the process of washing the bag with the sample was repeated 10 times before the final filling. The sample collected was analysed on a gas chromatograph HEWLLET-PACKARD model 5890 series II equipped with a *thermal conductivity detector* (TCD).

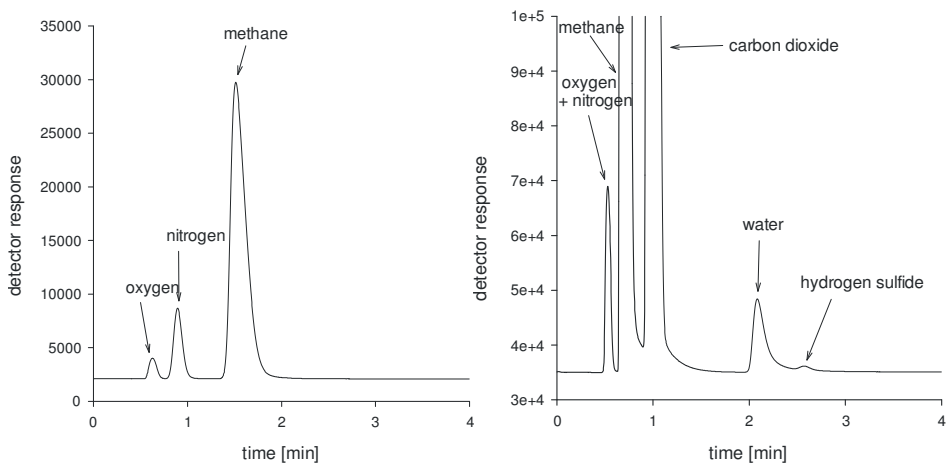

Fig. 3. Exemplary chromatograms revealing the sequence of elution of the components on the columns used. The chromatogram on the left was obtained on the column filled with molecular sieves 5 A, while that on the right on the column filled with HayeSep Q polymer

The sample of 0.3 cm^3 in volume was injected on the column with a gastight syringe. The components analysed were separated on two columns: one of 2.5 m in length and 1/8 inch in diameter filled with HayeSep Q polymer and the other of 1.5 m in length and 1/8 inch in diameter filled with molecular sieves 5A. The first column was used to determine the content of air, methane, carbon dioxide - in the low sensitivity mode and water and hydrogen sulphide - in the high sensitivity mode. The second column was used to determine the content of oxygen and nitrogen - in the high sensitivity mode. The separation was performed in isothermal conditions, at 75ºC for the column filled with molecular sieves and at 80ºC for the column filled with polymer. Exemplary chromatograms of the biogas analysed are presented in Figure 3.

Results and discussion

The monitoring of biogas composition was performed at the Central Wastewater Purification Plant for Poznan, in Kozieglowy (Table 2).

Table 2

Comparison of the biogas composition determined by GA2000 analyser and gas chromatography

Sample labelling (date of collection)	**GA2000**				**GC**				
	Component determined *								
29.03.2010	O_2	CH_4	CO_2	H_2S	O_2	N_2	CH_4	CO_2	H_2O
Bioreactor 18.1	0.0	60.7	38.3	68	0.1	0.4	58.9	39.3	1.3
Bioreactor 18.2	0.0	61.9	36.8	21	0.2	0.8	60.3	37.8	0.9
Bioreactor 18.3	0.0	62.5	37.1	29	0.1	0.4	61.1	37.7	0.7
Bioreactor 18.4	0.0	61.9	37.8	69	1.3	5.9	55.2	36.6	1.0
Bioreactor 18.5	0.0	61.9	37.2	15	0.1	0.7	60.2	38.2	0.8
Bioreactor 18.6	0.0	62.4	38.0	44	0.1	0.4	59.3	39.4	0.8
Before desulphur. chamber	0.0	61.8	37.8	67	0.2	0.5	60.1	38.3	0.9
After desulphur. chamber	0.0	61.8	37.5	45	0.1	0.6	60.5	38.1	0.7
Before power generator	0.0	61.6	38.2	13	0.2	0.8	59.6	38.6	0.8
01.07.2009									
Bioreactor 18.1	0.1	60.8	37.9	162	0.1	0.2	60.5	37.9	1.3
Bioreactor 18.2	0.4	52.0	33.7	122	3.2	12.3	50.7	32.5	1.3
Bioreactor 18.3	0.1	61.9	37.6	12	0.1	0.3	61.1	37.2	1.3
Bioreactor 18.4	0.1	62.1	37.3	117	0.1	0.2	61.7	36.6	1.4
Bioreactor 18.5	0.0	61.3	37.2	0	0.3	1.6	59.9	36.8	1.4
Bioreactor 18.6	0.1	62.7	36.4	190	0.1	0.3	62.4	36.0	1.2
Before desulphur. chamber	0.2	61.3	37.7	163	0.2	0.7	60.6	37.0	1.5
After desulphur. chamber	0.3	61.1	37.7	30	0.3	1.0	60.3	36.8	1.6
Before power generator	0.5	59.9	37.9	0	0.5	1.8	59.4	36.9	1.4
01.07.2008									
Bioreactor 18.1	0.2	58.9	37.8	86	0.1	0.1	60.4	38.8	0.6
Bioreactor 18.2	0.2	58.9	37.7	97	0.1	0.2	60.3	38.8	0.6
Bioreactor 18.3	0.2	58.1	38.5	61	0.1	0.3	60.4	38.6	0.6
Bioreactor 18.4	0.1	59.9	36.9	71	0.1	0.6	61.3	37.3	0.7
Bioreactor 18.5	0.1	59.4	37.1	26	0.1	0.4	61.1	37.9	0.5
Bioreactor 18.6	0.2	58.6	36.5	26	0.2	1.1	61.3	36.8	0.6
Before desulphur. chamber	0.0	59.9	37.6	63	0.1	0.3	60.9	37.9	0.8
After desulphur. chamber	0.0	59.9	37.4	25	0.1	0.3	61.6	37.5	0.5
Before power generator	0.1	59.2	37.8	21	0.2	0.6	60.5	38.1	0.6

* - concentration of all components except H_2S is given in volume %, the content of H_2S is given in ppm

Biogas was collected at a few sites to get the information on its composition in the process of formation and later its use as energy source. The lack of data for water and nitrogen among the determinations by GA2000 is a consequence of impossibility of their determination by the analyser of this type. Similarly it was impossible to determine the content of hydrogen sulphide on the gas chromatograph as the LOD of the analytical system (HayeSep Q filled column and TCD detector) was 300 ppm and in the biogas samples studied hydrogen sulphide occurred at lower contents. Comparison of the results of determinations shows that the difference between the results obtained by the analyser and those obtained by gas chromatography was at a level of 1.0÷1.5% for methane and 0.5÷1.0% for carbon dioxide. These results are much better than 3.0% declared by the producer of the GA2000 analyser. Close agreement between the analyser indications and results of gas chromatography follows from a high quality of the reference standards that were prepared according to PEH (*close manufacturing tolerance*) to maintain the declared composition to the accuracy of 0.1% for methane and carbon dioxide and 1 ppm for hydrogen sulphide.

The use of reference mixtures of the highest quality ensured the close agreement of the results despite the fact that we used reference mixtures from two producers in the period of the study (2008-2010). The use of two mixtures was necessary as the stability of certified material of this type reaches only 2 years. The contents of CH_4 and CO_2 indicated by the analyser were usually slightly overestimated with respect to chromatographic determinations, while the content of O_2 was always a bit lower than indicated by GC. The differences follow from the specific method of sample collection for GC analysis, which makes it impossible to totally remove air from the bags during the filling.

Conclusions

1. The agreement between the GA2000 analyser indications and GC results was at a level of 1.0÷1.5% for methane and 0.5÷1.0% for carbon dioxide, so better than 3.0% declared by the producer.
2. The high quality of the reference mixtures used, prepared according to PEH (close manufacturing tolerance) had important effect on the agreement between the GA2000 analyser and GC chromatography data.

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MONITORING BIOGAZU JAKO ŹRÓDŁA ENERGII ODNAWIALNEJ

Zakład Chemii Analitycznej, Wydział Chemii, Uniwersytet im. A. Mickiewicza, Poznań

Abstrakt: Biogaz to mieszanina różnych gazów, wśród których dwie trzecie stanowi metan (CH_4), jedną trzecią ditlenek węgla (CO_2). Pozostałe składniki nieorganiczne, organiczne i para wodna występują w biogazie w ilościach śladowych. W pracy przedstawiono wyniki badań dotyczących oznaczania składu ilościowego za pomocą popularnego przenośnego analizatora biogazu, jakim jest GA2000, w którym odczyt zawartości metanu i ditlenku węgla odbywa się metodą spektrofotometryczną, natomiast poziom tlenu i siarkowodoru elektrochemicznie. Otrzymane wyniki weryfikowano za pomocą chromatografii gazowej.

Słowa kluczowe: biogaz, chromatografia gazowa, analizatory biogazu, weryfikacja pomiarów

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BIOTECHNOLOGY OF THE FOOD INDUSTRY WASTEWATER TREATMENT FROM NITROGEN COMPOUNDS

BIOTECHNOLOGIA USUWANIA ZWIĄZKÓW AZOTU ZE ŚCIEKÓW PRZEMYSŁU SPOŻYWCZEGO

Abstract: Wastewater of food industries contains high concentrations of nitrogen compounds, mainly in the form of ammonium nitrogen. Traditional technological lines are able to reduce ammonium nitrogen about 80÷90%, but the desired concentration of nitrates in treated water for the standards of water use are not provided. The respective disadvantages of traditional lines are: the use of expensive chemicals (methanol and ethanol), large size of devices and buildings, large oxygen demand to the nitrification process, and required recirculation piping at each stage of technological line. The effective anaerobic-aerobic treatment technology of nitrogen compounds for food industry wastewater is proposed. The laboratory installation consisting of 5 bioreactors in series was designed. Biotechnology based on consistently jointed anaerobic and aerobic bioreactors with carrier for microorganisms immobilization was suggested. Hydrobiological biocenosis composition was also analyzed during the study. Construction and process parameters of laboratory installation were presented. The proposed technology of wastewater treatment of organic and nitrogen compounds allows to reach the levels of 98% such contaminants removal.

Keywords: wastewater treatment, food industry wastewater, nitrogen compounds, anaerobic-aerobic treatment, microorganisms immobilization

Almost all industrial and domestic wastewater contain both organic and inorganic nitrogen. The problem of nitrogen compound removal was developed in connection with deterioration of water quality in rivers and lakes, as the result of eutrophication. It gives place to excess amount of biogenous substance in the surface water. In its turn, this causes intensified growth of algae's other water plant and macrophytes. These water flora reduce the amount of incoming light into the basin depth, consume the dissolved oxygen and lead to the destructions of fauna and total disappearance of fish. In addition, water supply system is generally not equipped to remove nitrogen. Thus nitrogen compounds may income to the consumer and cause various diseases (cardiovascular, metabolic, etc.), even if consumed in small quantities. The above facts explain the increased requirements to ensure removal of nutrients especially nitrogen compounds from wastewater.

Nitrification process in combination with subsequent denitrification is still considered as the most common method of biological wastewater treatment. This method allows to remove ammonium nitrogen at 80÷90%, but do not provide the desired concentration of nitrates in treated water for the standards of water use. There are a number of disadvantages: expensive chemicals (methanol and ethanol), large size of WWTP devices and buildings, large oxygen demand to the nitrification process, and required recirculation piping at each stage of technological line.

Over the last 15 years in wastewater treatment technology, several new processes of nitrogen compounds removal have been created: CANON (*Completely Autotrophic*

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Nitrogen removal Over Nitrite), OLAND (*Oxygen Limited Autotrophic Nitrification Denitrification*), SHARON-ANAMMOX (*Single reactor High activity Ammonia Removal Over Nitrite - ANaerobic AMMonium OXidation*), DEAMOX (*Denitrifying Ammonium Oxidation*) [1]. Among the most modern technological schemes that allow to remove nitrogen compounds A/O, A^2/O, An/O, Bardenpho, UCT, Biodenipho processes, Carousel scheme (simultaneous method), JHB, and others, can be marked [2]. External and internal recirculation of flow are used and is one of the main disadvantages of the above schemes and technological processes.

Anaerobic processes in traditional biological technology are recently used for anaerobic sludge stabilization (in clarifies, septic tanks, digestion tank). Today, the biological wastewater treatment with high level of nitrogen removal in anaerobic conditions is widely used worldwide and this trend is observed in practice. Anaerobic technologies have certain undeniable advantages in comparison with aerobic [3].

After the biological wastewater treatment in anaerobic condition necessarily to aerobic advanced treatment occur. However, it requires a much lower cost than the only aerobic wastewater treatment. The low rates of growth and slow metabolism of the microorganisms removing nitrogen compounds lead to increase the activated sludge age to achieve their proper concentration in bioreactor. This problem can be solved by using of anaerobic and aerobic bioreactors with microorganisms immobilization. System with immobilized microorganisms does not require for wastewater recirculation. Immobilization of microorganisms cells allows for complex multistage process, causes better protection of cells from the action of extreme factors, and creates a high concentration of cells in the reactor. In addition, immobilized microorganisms are often less sensitive to toxic substrates.

The objective of our researches is to intensify the process of biological wastewater treatment, including food industry, of nitrogen compounds by technological line with immobilized microorganisms.

Materials and methods

For the food industry wastewater treatment, the anaerobic-aerobic biotechnology was applied. The laboratory installation was composed of five bioreactors. The anaerobic and aerobic reactors have 1 dm^3 of effective volume, respectively. Carrier height was 0.17÷0.235 m, diameter of fiber - 3 mm, number of fiber in one carrier 142÷98 units. The wastewater from milk plant and malt factory was chosen for the research. Investigation was carried out separately on different plants, similar in composition and work.

The concentration of pollution in milk plant wastewater is characterized by: *Chemical Oxygen Demand* (COD) 1000÷5000 g m^{-3}, *Biochemical Oxygen Demand* (BOD_5) 700÷3700 g m^{-3}, total nitrogen 20÷170 g m^{-3}. Model solution was prepared for a milk plants sewage simulation. Concentration of ammonium nitrogen was 45÷58 g m^{-3}, pH 6.5÷6.8. Wastewater of malt factory was generated in the process of soaking and germination malts and contain: COD 1760÷4000 g m^{-3}, BOD_5 1400÷2000 g m^{-3}, total nitrogen 30÷80 g m^{-3}, suspended solids concentration of 350÷600 g m^{-3}, pH 6.0÷7.5. The solution used for researches was consist of wastewater from malt factory of Slavuta, Ukraine. The concentration of ammonium nitrogen about 25÷40 g m^{-3}, suspended solids: 510÷580 g m^{-3}, pH 6.0÷6.3.

As a precursor for increase the biomass in bioreactors was used activated sludge from Slavuta municipal wastewater treatment plant. The carriers made of artificial fibers of the VIYA (Eyelash) type were used for microorganisms immobilization. After starting the experiment, on the "VIYA" the amount of microbial biomass in the anaerobic and aerobic bioreactors was gradually increase. The process of increasing biomass has reached the maximum level at 45 day [4].

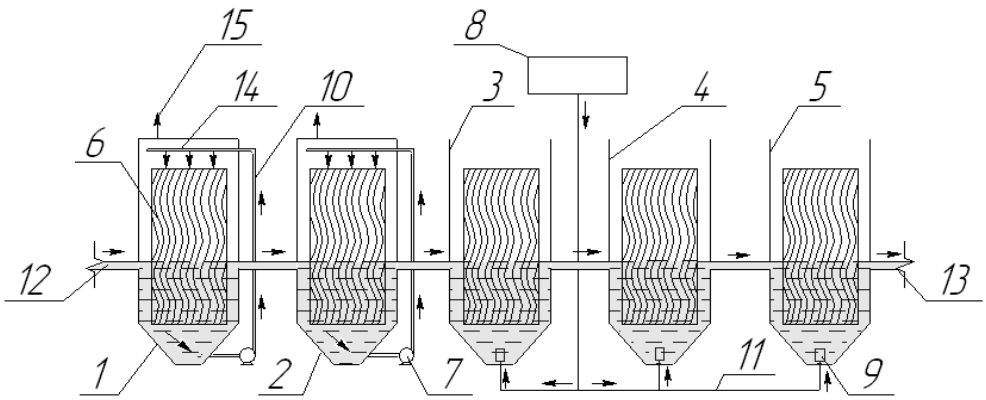

Fig. 1. Scheme of laboratory installation: 1, 2 - anaerobic bioreactors, 3, 4, 5 - aerobic bioreactors, 6 - fibrous carrier "VIYA", 7 - pump, 8 - compressor, 9 - aerator, 10 - irrigation piping, 11 - air line, 12 - supply pipeline wastewater; 13 - pipeline for the treated water, 14 - perforated pipe, 15 - a device for collecting gas

Operation of the laboratory installation may be described as follows (numbers in brackets are connected with scheme presented at Figure 1): Wastewater pass by anaerobic section (1). Then wastewater passes through fibrous carrier “VIYA” (6) and contacts with immobilized microorganisms on it. Irrigation is conducted by the circulating pump (7). Process in anaerobic bioreactor (1) proceeds with allocation of gases, collected by the device for gathering of gas (15), and development of anaerobic bacteria which are kept on fibers of the carrier (6). The water treated thus gets in following anaerobic bioreactor (2) where occur a similar process differed only by specific structure of microorganisms biocenosis, which change under the influence of spatial microorganisms succession. Then wastewater flows consistently by aerobic bioreactors (3, 4, 5) in which from the compressor (8) connected with an air pipe (11) air is pressed in regular intervals to be distributed in the form of small air bubble through aerators (9). In all aerobic bioreactors fibrous carriers (6) on which the microorganisms with specific structure shaped by process condition of sewage treatment also are located. The pipeline (13) takes the cleared wastewater out of installation.

The number of variants was considered for the choice of the most effective carrier material for microorganisms immobilization. The artificial fibers “VIYA” selected to role of carrier, has a following advantages: the large specific surface for biocenose fastening and

insolubility in water. It is also characterized by high durability and firmness to microbe destruction and is not harmful to microorganisms [5].

Results and discussion

Using the first two stages of installation connected with anaerobic process (first and second bioreactors) allows the removal of organic pollutants. Stirring was conducted with circulating pump. In anaerobic bioreactors, treatment process takes place without oxygen and with the selection of gases, which collect specific device.

The third bioreactor of wastewater treatment occurs with air supply, but the conditions in the reactor are anoxic (shortage of oxygen). After passing the wastewater through anaerobic bioreactor, the concentration of organic matter significantly reduced, and that causes the first stage of nitrification. In deeper layer of fiber carrier, with no oxygen, but enough organic matter, denitrification can also occur. In this bioreactor, ANAMMOX-process is possible at high concentrations of ammonium compounds (> 0.2 g m^{-3}) and low concentrations of organic carbon [6].

The fourth and fifth bioreactor is saturated by air from the compressor that provides aerobic conditions. There is a second stage of nitrification. Immobilized microorganisms conduct the biological oxidation of pollutants which clean wastewater from all forms of nitrogen, with minimum amount of excess sludge which is characterized by good dewatering and low humidity.

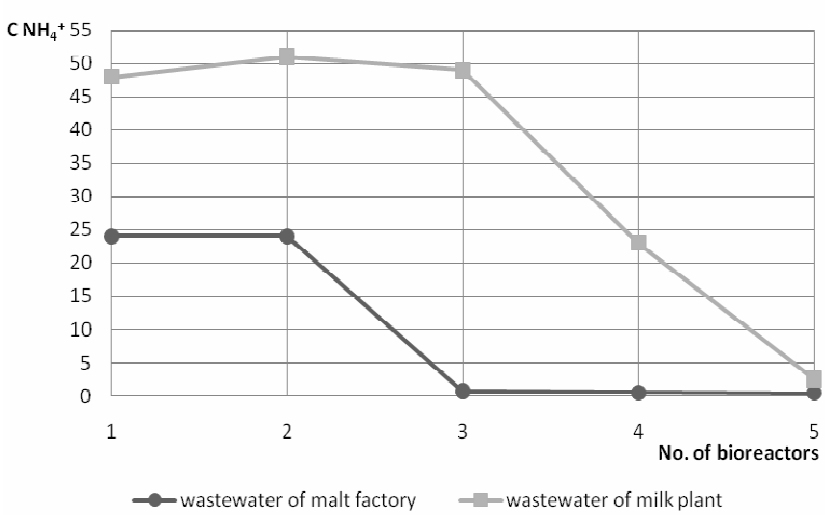

Fig. 2. Changes in the concentration of ammonium nitrogen of food industry wastewater after passing by five following bioreactors

The efficiency of ammonium nitrogen removal from dairy wastewater and malt wastewater, which is 98.5% and 98% respectively (Fig. 2) was achieved. Sampling of sewage for investigation was conducted at the inflow to each bioreactor.

Summary and conclusions

Based on the conducted experiment with the implementation of anaerobic-aerobic technology with immobilized microorganisms it is possible to make the following conclusions:

- Due to immobilization of microorganisms connected which their concentration in small volumes of a construction the reduction of bioreactor capacity is possible.
- Increase in concentration of a biomass allows to reduce duration of wastewater treatment.
- Constant and high concentration of biomass as well as lack of their recirculation between bioreaction chamber and absence of aeration in two chambers allow to reduce quantity of the used electric power.
- The sediment received from the last bioreactor is in small amount, dewaters well and is characterized by low humidity (90%).
- The presented technology allows to reach high level (98%) of wastewater treatment from organic matters and nitrogen compounds. It can be applied to food-processing industry wastewaters.

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BIOTECHNOLOGIA USUWANIA ZWIĄZKÓW AZOTU ZE ŚCIEKÓW PRZEMYSŁU SPOŻYWCZEGO

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Abstrakt: Ścieki z przemysłu spożywczego mają wysokie stężenia związków azotu, w tym głównie azotu amonowego. Tradycyjne linie technologiczne umożliwiają obniżenie stężeń azotu amonowego o około 80 do 90%. Jednakże uzyskiwane stopnie usunięcia związków azotu z oczyszczanych ścieków przemysłu spożywczego nie spełniają standardów pozwalających na ich bezpośrednie odprowadzenie do wód odbiornika bądź też powtórne wykorzystanie. Ponadto przy zastosowaniu tradycyjnych schematów technologicznych pojawia się szereg niedogodności. Do ważniejszych z nich można zaliczyć konieczność okresowego zastosowania kosztownych związków chemicznych (np. metanolu lub etanolu) oraz duże rozmiary urządzeń i objętości komór oczyszczania. Wymagane znaczne strumienie powietrza niezbędne w prowadzeniu procesu nitryfikacji, a także konieczność wykorzystania pomp i przewodów recyrkulacyjnych w odpowiednich punktach linii technologicznej powodują wzrost kosztów energii elektrycznej. W celu uniknięcia wspomnianych niedogodności zaprojektowano przedstawioną w ramach niniejszej pracy beztlenowo-tlenową technologię biologicznego oczyszczania ścieków z przemysłu spożywczego. Opracowana instalacja laboratoryjna składa się z pięciu połączonych szeregowo bioreaktorów. Poprzez wykonanie poszczególnych sekcji bioreaktorów uzyskano możliwość oczyszczania

ścieków w systemie przepływowym bez konieczności recyrkulacji pomiędzy sekcjami. Mikroorganizmy osadu czynnego wykorzystywane podczas biologicznego oczyszczania ścieków mogą także zasiedlać zamontowane w tym celu wypełnienie z nośników w postaci włókien, co służy zwiększeniu koncentracji biomasy w bioreaktorze. W ramach prowadzonego eksperymentu badano parametry procesowe instalacji laboratoryjnej oraz skład biocenozy saprobów zasiedlających bioreaktory. W wyniku prowadzonych procesów oczyszczania udało się osiągnąć obniżenie stężenia związków azotu na poziomie 98%.

Słowa kluczowe: oczyszczanie ścieków, ścieki przemysłu spożywczego, związki azotu, oczyszczanie tlenowo-beztlenowe, immobilizacja mikroorganizmów

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DEVELOPMENT AND ACTIVATION OF THE SECOND TECHNOLOGICAL PIPE IN THE WASTEWATER TREATMENT PLANT IN DOBRON

ROZBUDOWA I URUCHOMIENIE DRUGIEJ LINII TECHNOLOGICZNEJ W OCZYSZCZALNI ŚCIEKÓW W DOBRONIU

Abstract: The aim of the investigation was characterizing and operation assessment of the municipal wastewater treatment plant in Dobron, taking into consideration its current flow capacity (700 m^3/d) after development including building of the second similar technological pipe with the same flow capacity (350 m^3/d), finished in September, 2009. Concise description of the applied wastewater treatment technology and results of investigations concerning flow rates of wastewater within last few years, are presented. Example results of wastewater composition analysis before and after the treatment process are shown. Moreover, amounts of wastes (screenings, sand and stabilized sludge) formed in the wastewater treatment process, are presented.

Keywords: Ecolo-Chief type wastewater treatment plants, phosphorus and nitrogen reduction in wastewater

Industrial and municipal wastewater generated during new investments realization as well as development of sewerage systems in villages and towns causes the necessity of building of new wastewater treatment plants and development of existing ones. These plants include conventional mechanical and biological treatment methods (1st and 2nd stage) and guarantee removal of biogenic compounds, ie, nitrogen and phosphorus, in the third stage of treatment [1-5].

Ecolo-Chief type wastewater treatment plants are process lines designed and produced by CHIEF INDUSTRIES, INC. (Nebraska, USA). The wastewater treatment system was modernized by Multibranch PPU Sumax, Inc. (Krakow) within the range of biogenic compounds removal and secondary settling tank operations. About 75 wastewater treatment plants using this technology, have been built in Poland [5, 6].

Experimental

The aim of the investigation was characterizing and operation assessment of the wastewater treatment plant in Dobron taking into consideration its flow capacity (Q), before (~350 m^3/d) and after development including building of the second technological pipe with the same flow capacity (350 m^3/d), finished in September, 2009 (Fig. 1). Concise description of the applied wastewater treatment technology and results of investigations concerning flow rates of wastewater within last few years, are presented below. Wastewater treatment plant in Dobron (Ecolo-Chief type) operates according to the technology of low-loaded activated sludge with aerobic sludge digestion [6-8]. The wastewater treatment plant after the development includes the following systems:

- 1 drainage point of supplied wastewater with storage reservoir,
- 1 wastewater pumping station with basket screen,

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- 2 sand traps,
- 2 primary settling tanks,
- 2 oxygen deficiency tanks (anoxic),
- 8 aeration tanks,
- 2 tanks of aerobic sludge digestion,
- 2 secondary settling tanks,
- 2 wastewater wells for measurement of wastewater flow,
- 2 set of rotary blowers.

Technological system for sludge treatment consists of:

- 2 tanks of aerobic sludge digestion,
- 1 sludge pumping station,
- 1 tape press for mechanical removal of sludge (sludge dewatering).

Fig. 1. The view of the developed wastewater treatment plant in Dobron

Ecolo-Chief type wastewater treatment makes an increase in the main unit efficiency by combination of particular modules, possible. This is important especially during development of sludge units and gradual increasing of disposed wastewater amount, what concerned the municipal wastewater treatment plant in Dobron. This system operates perfectly in such objects where seasonal wastewater dump (for example in summertime) significantly exceeds the average dump in the other months. An application of the treatment system with periodical recirculation of a part of wastewater and sludge causes that all system operates under the condition of a full pollutants load also in the period of lower wastewater supply.

Results and discussion

Data concerning amounts of wastewater received in the wastewater treatment plant, pollutants loads and formed technological wastes (screenings, sand removed from sand

traps and stabilized sludge) are presented in Tables 1-3. Example results of analysis wastewater composition, before and after the treatment process are shown in Tables 4.

Table 1

Annual volumes of wastewater supplied to the wastewater treatment plant in Dobron over the period from 1999 to August, 2010 [9, 10]

Year	**Q [m^3/year]**
1999	41100
2000	50010
2001	61116
2002	51369
2003	59179
2004	60515
2005	71794
2006	70526
2007	78647
2008	87818
2009	93304
I-VIII 2010	92462

Table 2

Daily average load of pollutants supplied to the wastewater treatment plant in Dobron over the period of 2007-2009 [9, 10]

Indicator name	**Concentration [g O_2/m^3 or g/m^3]**	**Pollutants load [kg/day]**
BOD_5	247	67.9
COD-Cr	511	140.5
Total nitrogen	86.2	23.7
Total phosphorus	10.4	2.9
Total suspended solids	222	61

Table 3

Waste types and amounts per month in 2009 and over the period of I-V 2010 [10]

Year/Month	**Waste types and amounts [Mg/month]**		
2009	**Screenings**	**Sand traps contents**	**Stabilized sludge**
January	0.53	0.2	4.16
February	0.43	0.3	8.44
March	0.3	0.2	8.8
April	0.48	0.4	7.74
May	0.43	0.3	13
June	0.39	0.33	9.82
July	0.52	0.3	6.44
August	0.42	0.4	8.94
September	0.47	0.31	7.3
October	0.44	0.5	13.2
November	0.42	0.4	15.3
December	0.42	0.4	11.44
2009 Total	**5.25**	**4.04**	**114.58**
January	1.08	0.6	3,24
February	1.1	0.5	7,98
March	1.08	0.8	6,22
April	1.05	0.8	7,92
May	1.0	0.6	8,22
2010 I-V Total	**5.31**	**3.3**	**33.58**

Increasing amount of the wastewater supplied by sewerage and by waste removal transport, and their load caused to take a decision about development of the wastewater treatment plant in Dobron (Tables 1 and 2). Before the development, plant loading was gradually approaching to the limit of its maximum loading (350 m^3/d), especially in the period of increased wastewater supply. Beginning from September, 2009, the plant can treat the wastewater amount of 700 m^3/d. The increased flow capacity in this plant can guarantee the achievement of satisfied operation indicators for at least several years. Composition of the wastewater supplied to Palusznica river does not cause any quality reservations and fulfils law requirements [11, 12]. This plant is not hazardous for inhabitants taking into consideration odours, due to the applied treatment technology and favourable location. This is proved by lack of inhabitants' complaints about the plant operation. Up to now, no hazard of the plant to the quality of underground and surface water was found. Solid wastes (screenings, sand from sand traps and stabilized sludge) are carried outside the plant to another firm in order to utilize them.

Table 4

Examples of composition analyses in raw and treated wastewater over the period of 2008-2010 [10]

Date of wastewater sampling	Contamination indicator in raw and treated wastewater			
	pH	BOD_5	COD-Cr	Total suspended solids
	[-]	[mg O_2/dm^3]	[mg O_2/dm^3]	[mg/dm^3]
16.05.2008	7.4/7.4	682/10	1109/56.4	241/20
21.11.2008	7.4/7.1	319/2.7	550/17	133/14
05.02.2009	7.8/7.1÷7.3	485/8.1	804/52	34/11
14.05.2009	7.6/7.2÷7.3	739/18.0	1246/105	763/18
13.08.2009	8.0/7.8÷8.4	695/9.0	1171/45	120/13
03.11.2009	-/7.4÷7.6	-/7.03	-/40	-/6.0
16.02.2010	7.5/7.3	610/15.9	1022/72	230/6.0
10.06.2010	6.6/7.1	466/11.6	826/57	388/15
30.08.2010	7.6/7.3	366/13.8	633/64	349/5.0

Conclusions

The increased flow capacity of the plant to 700 m^3/d guarantees the achievement of satisfactory operation indicators. The plant operation is not odour hazardous for inhabitants due to its proper location to other buildings (lack of inhabitants' complaints). No hazard to the quality of surface and underground waters resulting from the treatment plant operation was found so far. Solid wastes formed during the technological process of the wastewater treatment (screenings, sand from sand traps and stabilized sludge) are disposed outside the plant in order to utilized them.

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[11] Rozporządzenie Ministra Środowiska z dnia 8 lipca 2004 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub do ziemi oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego. DzU 2004, Nr 168, poz. 1763.
[12] Rozporządzenie Ministra Budownictwa z dnia 14 lipca 2006 r. w sprawie sposobu realizacji obowiązków dostawców ścieków przemysłowych oraz warunków wprowadzania ścieków do urządzeń kanalizacyjnych. DzU 2006, Nr 136, poz. 964.

ROZBUDOWA I URUCHOMIENIE DRUGIEJ LINII TECHNOLOGICZNEJ W OCZYSZCZALNI ŚCIEKÓW W DOBRONIU

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Abstrakt: Celem pracy była charakterystyka i ocena funkcjonowania oczyszczalni ścieków komunalnych gminy Dobroń o przepustowości obecnej (700 m^3/d), po jej rozbudowie o drugą (analogiczną do istniejącej) nitkę technologiczną (350 m^3/d), sfinalizowaną we wrześniu 2009 r. Oprócz zwięzłego opisu realizowanej technologii oczyszczalnia ścieków przedstawiono wyniki badań natężenia ich przepływu z ostatnich kilku lat. Ukazano także przykładowe rezultaty analizy składu ścieków przed i po procesie ich oczyszczania. Ponadto podano ilości powstających odpadów (skratki, piasek i ustabilizowany osad ściekowy) w procesie oczyszczania ścieków.

Słowa kluczowe: oczyszczalnie typu Ecolo-Chief, redukcja fosforu i azotu w ściekach