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CHANGES OF PAHs CONCENTRATION IN SEWAGE SLUDGE MODIFIED BY $ZnCL_2$

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ZMIANY STĘŻEŃ WWA W OSADACH ŚCIEKOWYCH MODYFIKOWANYCH $ZnCL_2$

Celem badań było ustalenie, w jakim stopniu obecność cynku, na poziomie granicznej zawartości określonej dla osadów stosowanych w rolnictwie (przekraczającej zawartość oznaczoną w osadach odprowadzanych z oczyszczalni), wpływała na zmiany zawartości WWA w tych osadach przechowywanych w warunkach tlenowych. Badania prowadzono z wykorzystaniem osadów ustabilizowanych biochemicznie i odwodnionych. Zmiany stężeń WWA śledzono równolegle w czterech seriach: osadach pobranych z oczyszczalni (po prasach filtracyjnych), osadach z dodatkiem mieszaniny wzorcowej, z dodatkiem cynku oraz z dodatkiem mieszaniny wzorcowej i cynku. Wykorzystano mieszaninę standardową PAH Mix 16 związków w benzenie i dichlorometanie (1:1). Cynk wprowadzano do osadów w postaci roztworu chlorku cynku, po uwzględnieniu zawartości początkowej, w takiej ilości, aby zawartość końcowa nie przekraczała 2500 mg Zn/kg s.m. Osady inkubowano przez 90 dni w temperaturze 20°C przy nieograniczonym dostępie tlenu. Oznaczenia WWA przeprowadzono na początku doświadczenia (zawartość początkowa), po 15, 30, 45, 60, 75 i 90 dniach każdorazowo w dwóch powtórzeniach. Oznaczenia jakościowo-ilościowe WWA prowadzono z wykorzystaniem zestawu GC-MS. Identyfikowano 16 WWA zgodnie z listą US EPA.

Summary

The aim of the investigation was to determine the impact of the presence of Zn in concentrations of sludges applied in agriculture (exceeding concentrations determined in sludges drained from the treatment plant) on the disappearance of PAHs in sewage sludge stored under aerobic conditions. The studies were carried out using dewatered and biochemically stabilized sludges. The changes in the concentration of PAHs were studied in four series: in sludge samples taken after filter press, in sludge with the addition of a standard PAH mixture, in sludge with Zn added, in sludge with the addition of both the standard PAH mixture and Zn. The standard PAH mixture used in the studies contained 16 compounds in benzene – dichloromethane (1:1) solution with a concentration of 32000 $\mu g/cm^3$ of 16 PAHs. Zn was added to the sludge samples as a solution of chloride zinc, the final amount was below 2500 mg Zn/kg d.m. (taking into consideration the initial concentrations). The sludge samples were incubated for 90 days at 20°C with limitless access of oxygen. The determination of PAHs in sludge samples was done in duplicates at the beginning of the experiment (the initial concentration) and then six times at 15-day intervals (after 15, 30, 45, 60, 75 and 90 days). A gas chromatography-mass spectrometry (GC-MS) was used to qualify and quantify the PAHs. 16 PAHs listed by EPA were identified.

INTRODUCTION

It is stated in the literature that PAHs are not degradable enough but they may be subjected to fates forming PAHs-related compounds [1, 3, 6, 7]. PAHs are sorbed mainly onto organic matter particles. Strong sorption causes PAHs' accumulation in the environment [9, 13, 16, 17]. PAHs are regarded as xenobiotics relatively resistant to the decomposition process that depends on both abiotic factors and the presence of microorganisms [5, 15, 16]. The level of decomposition depends on physical-chemical hydrocarbon properties, environment (water, soil, air) and environmental conditions (humidity, temperature, light, pH of environment) [3, 12].

There have been a limited number of investigations concerning the impact of the occurrence or addition of some heavy metals on PAHs fates. Maliszewska-Kordybach *et al.* described research into the effect of zinc, lead and cadmium salts on PAHs persistence, but in the relation to a soil environment [11]. Lazzari *et al.* found a link between the presence of PAHs and mercury, cadmium, zinc and copper in composted sewage sludges [8]. In both cases it turned out that the presence of metals inhibited the disappearance of PAHs. This was due to the lower biological activity of bacteria responsible for the decomposition of these compounds [5, 7]. It was also found out that individual hydrocarbons had varied sensitivity when metals were presented [5]. The obtained results confirm the differential dependency between the concentration of individual hydrocarbons and the studied metals. A positive correlation between some metals (Cu, Cd, Zn, Pb) and chrysene and benzo(k)fluoranthene was found. Adsorption onto organic matter particles, biodegradation and, at a lower level, volatilization is regarded as the processes responsible for changes in PAHs concentration during composting. It was found out that the intensity of the above mentioned processes depends on the number of rings in the molecule [8]. The application of sewage sludge in agriculture is limited by permissible heavy metals concentrations [2]. Proposed changes to UE Directive demand the control of organic pollutants in sewage sludge applied in agriculture including PAHs, PCBs and AOX [14]. Sewage sludges originating from municipal treatment plants are usually loaded with both heavy metals and PAHs [4, 5, 14, 18]. Therefore, it is important to investigate the behavior of hydrocarbons during the storage of sewage sludges on the environment. In this study attention was paid to the determination of PAH changes dynamic in sewage sludges with zinc added. The experiments were carried out under aerobic conditions.

The objective of this work was to find out what impact the addition of zinc to concentrations exceeding permissible levels had on PAHs depletion in sewage sludges stored under aerobic conditions.

The following investigations were done:

- determination of changes in PAH concentrations in sewage sludge samples taken from municipal treatment plant,
- determination of changes in PAH concentrations in sewage sludge samples with zinc added,
- determination of changes in PAH concentrations in sewage sludge samples taken from a municipal treatment plant and supplemented with a standard mixture of these compounds,
- determination of changes in PAH concentrations in sewage sludge samples taken from municipal treatment plant and supported the standard mixture of these compounds as well as zinc.

EXPERIMENTAL SET-UP

The investigations were carried out under laboratory conditions using dewatered sludges formerly stabilized in a two-stage digestion process. Sludge samples were a one-off batch taken from a municipal treatment plant. The sludges were primarily analyzed for: humidity, pH, alkalinity, acidity, and contents of organic compounds, total zinc was also determined.

The sludge samples were homogenized by quartering to select a representative sample. Afterwards, fifty six samples of 10 g each were prepared, and were then put into 200 cm^3 glass flasks and protected from photovolitalization. A chloride zinc solution equal to 1500 mg of Zn/kg of dry matter (d.m.) (including original Zn concentration) was added to twenty eight sludge samples. A standard mixture of 16 PAH compounds in benzene and dichloromethane in the concentration of 2000 $\mu g/cm^3$ each was added to fourteen samples. The standard mixture dose was 10000 mg/kg d.m. The same dose of the standard mixture was also added to the fourteen remaining sludge samples. Samples without the addition of zinc as well as without the addition of the standard mixture were treated as control samples. All the samples were incubated for 90 days at a temperature of 20°C in the dark in order to limit photovolitalization but with no limits on access to oxygen. The whole volume of each sludge sample was used to determine PAHs. PAH samples were taken at the beginning of the experiment (the initial concentration) and six times at 15 day intervals (after 15, 30, 45, 60, 75 and 90 days). The humidity of the sludges was also determined at the same day intervals.

ANALYTICAL METHODS

The analysis of PAHs consisted of: separation of the organic matrix from the sludge, the isolation of hydrocarbons by extraction, chromatographic separation of these compounds and their qualification and quantification. An extraction process for sludge samples with cyclohexane and dichloromethane mixture (in the ratio 5:1 (v/v)) as a solvent was carried out in an ultrasonic bath for 40 minutes. Extracts were selected from sludge samples by centrifuging. The prepared extracts were primary concentrated under a nitrogen stream to a volume of 3 cm^3 and then purified by using SPE columns packed with silica gel formerly treated with the mixture of cyclohexane and dichloromethane. Then the purified extracts were again concentrated under a nitrogen stream to a volume of 1 cm^3. The gas chromatography-mass spectrometry (GC-MS) was used to qualify and quantify the PAHs. The separation was performed on a DB-5 column (30 m, 0.25 mm, 1.0 μm). The following temperature program was used: initially the oven was kept at 40°C, heated at 40°C per minute to 120°C and a final temperature of 280°C was obtained by heating at 40°C per minute for 32 minutes. The temperature of 280°C was held for 25 minutes and then the column was cooled to the initial temperature of 40°C. The analysis was carried out in the detector temperature of 200°C. Helium 0.5 cm^3/min was used as a carrier gas and the total analysis was held for 50–60 minutes. Sixteen PAHs on the US EPA list were analyzed. All analyses were performed in duplicate. In order to evaluate extraction method efficiency PAH recoveries from sludges were also determined. A standard mixture of 16 EPA-PAHs was added to sludge samples and the content of 16 hydrocarbons was determined according to the procedure described above.

RESULTS AND DISCUSSION

The sludges originating from a municipal treatment plant had a low water content (83%) associated with dewatered sludges formerly biochemical stabilized. The same was found for alkanity (55 mval/dm^3) and pH = 8.4. Organic matter content of 52% proved that the sludge was well digested. A comparison of the concentration of selected metals in sludges and the EU directive limits for municipal sludge in agriculture are presented in Table 1. The sludges had a low zinc concentration (422 mg/kg d.m.) and the concentrations of other metals were also below permissible levels for sludges applied in agriculture and recultivation areas assigned for agricultural purposes [2].

Table 1. Concentration of metals in sewage sludge

Sewage sludge	Concentration, mg/kg d.m.						
	Cu	Pb	Cd	Zn	Ni	Cr	Hg
Sewage sludge from treatment plant	149	15.6	1.0	422	38.3	102	0.31
Limit of metals concentration in sewage sludge [2]	800	500	10	2500	100	500	5

The recoveries of PAHs standard mixture for concentrations in sludges taken from the municipal treatment plant varied from 25% (naphthalene) to 94% (pyrene). The average value (taking into account the most volatilize naphthalene) was 65% which corresponds to data in the literature [5, 14]. The average total concentration of 16 PAHs in sludges taken from the municipal treatment plant was 1807 mg/kg d.m. which corresponds with the results of other authors as well as our own results [4, 14, 18]. The dynamics of hydrocarbon changes grouped according to ring numbers and the total sum of PAH concentration in the control sludges as well as those with zinc added (A) are given in Figures 1–6. The gradually lower concentration of the 16 PAHs studied was determined during incubation of the samples under oxygen conditions. At the same time fluctuations in naphthalene concentrations in the control sludges and in those with zinc added were observed. In the initial step of the investigation (after 15 days) the total PAHs concentration in the control sludges and sludges with Zn added was lower than in the initial ones by 7% and 3%, respectively. 2.7- and 1.7-times higher naphthalene concentrations were found in the control sludges and in the sludges with added Zn, whereas a 35% and 26% decrease in 5-ring hydrocarbons occurred. Fluctuations in naphthalene concentrations may occur due to its periodic appearance as an indirect product of the decomposition of other complex PAHs [10]. Within the following four weeks (after 45 days) of incubation of the sludges the total PAH concentration was similar in the control sample and in the sludge with Zn added (1576.5 mg/kg d.m. and 1596.9 mg/kg d.m.). Simultaneously, fluctuations in 5 and 6-ring PAH concentrations were observed. Significantly lower PAH concentrations were found after further incubation time, mainly in the control sludges. The total PAH concentrations were 42% and 72% lower than the initial one after 60 and 75 days, respectively. The same tendency was observed in the sludge samples with zinc added; after 60 days and 75 days the total PAH concentrations were 18% and 34% lower than the initial one, respectively. The decrease in 3-ring hydrocarbons in the control sludges and in those with zinc added was similar to the initial concentration and was 41% and 44%, respectively. The percentage decrease in other hydrocarbons was from 2-times up to 4-times lower in the sludge samples with zinc added than in the control samples. 5- and 6-ring hydrocarbons in the presence of Zn proved especially resistant. The final concentrations of 5 and 6-ring PAHs in control samples were 82–84% lower than the initial ones, whereas they were 52% and 62% lower for the modified sludges, respectively.

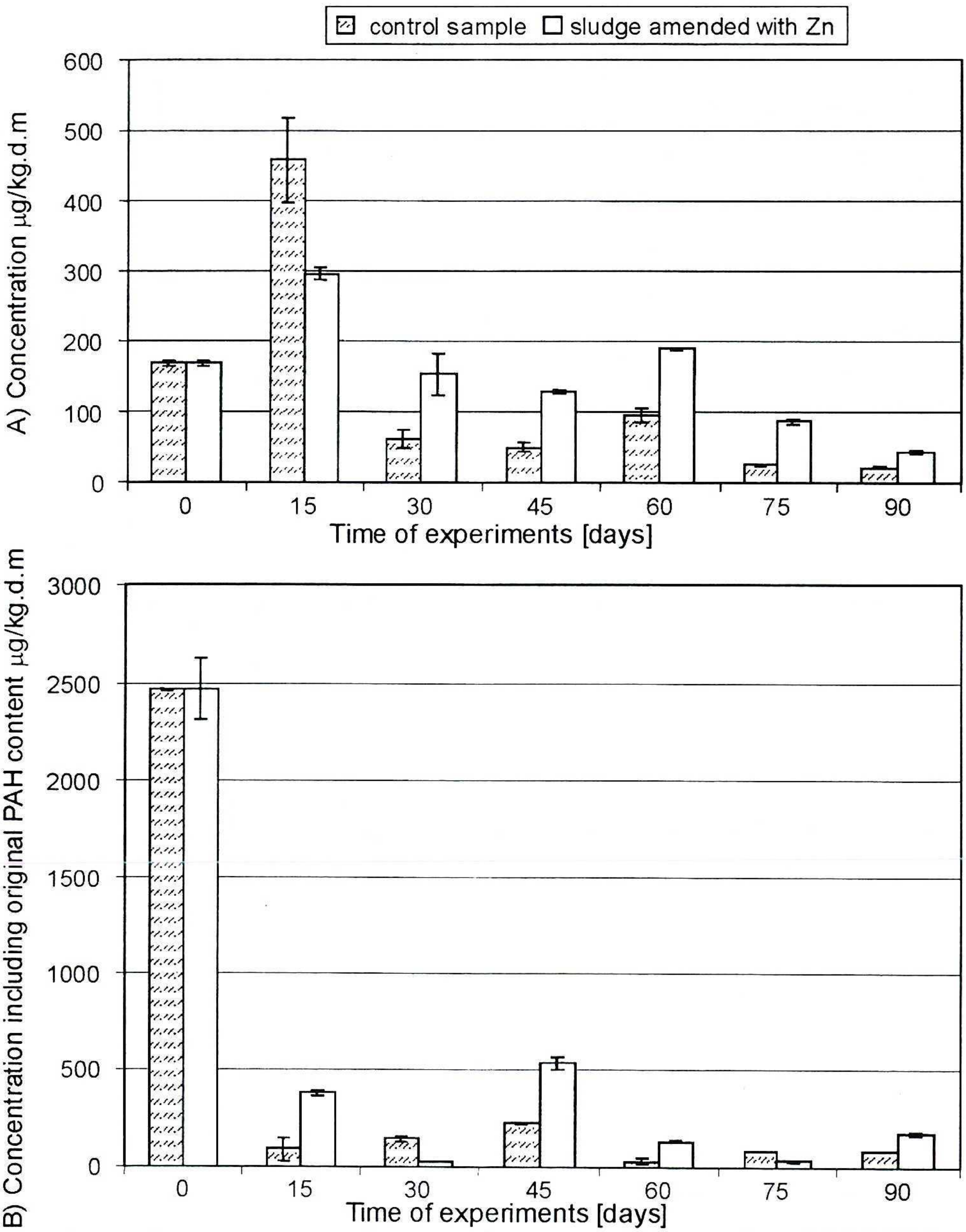
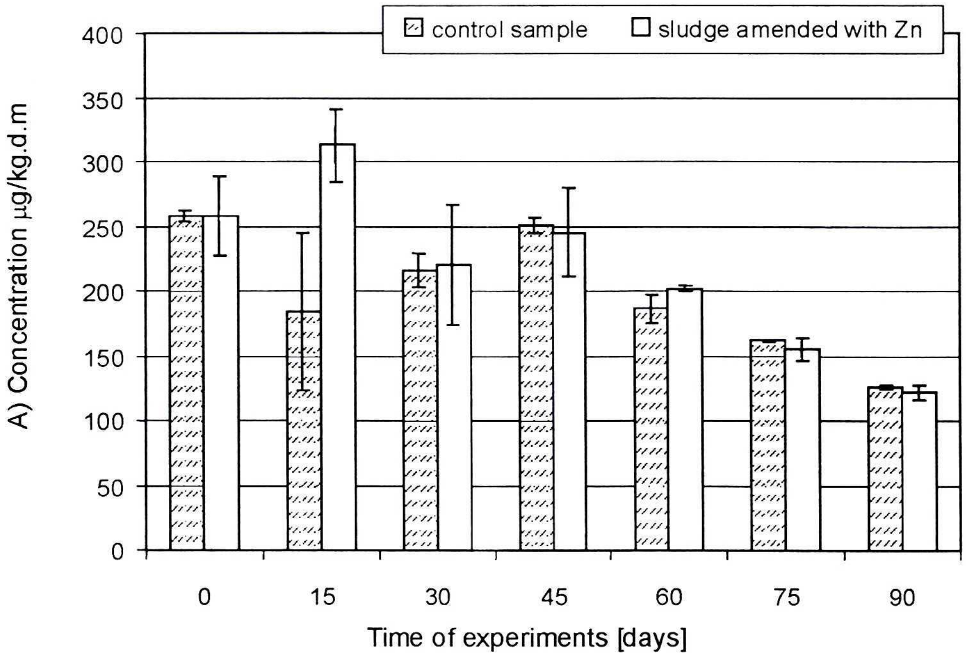


Fig. 1. Changes in naphthalene concentration in sewage sludge A) control sample, B) with a standard mixture



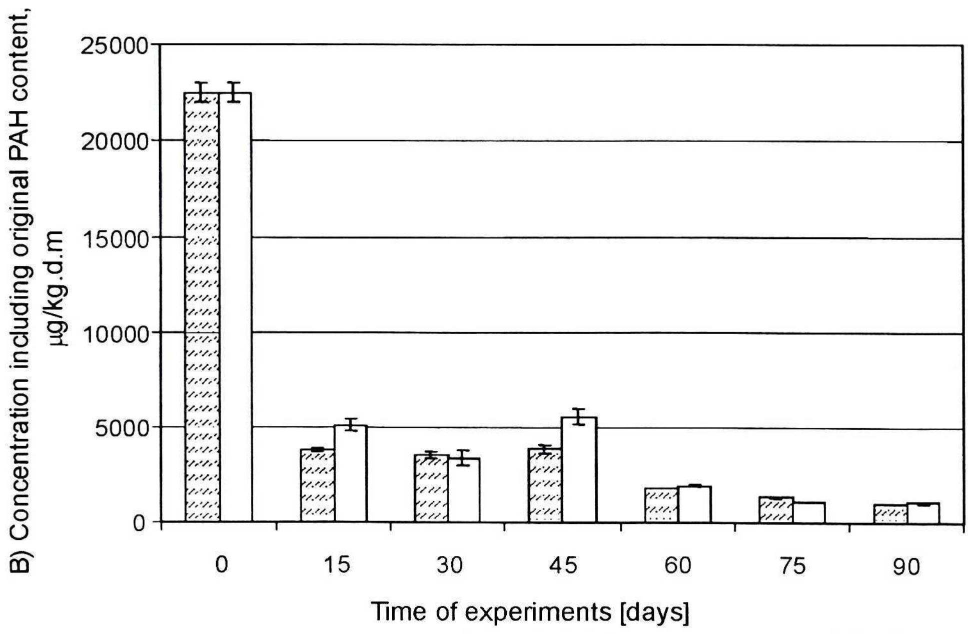


Fig. 2. Changes in 3-ring PAH concentrations in sewage sludge A) control sample, B) with standard mixture

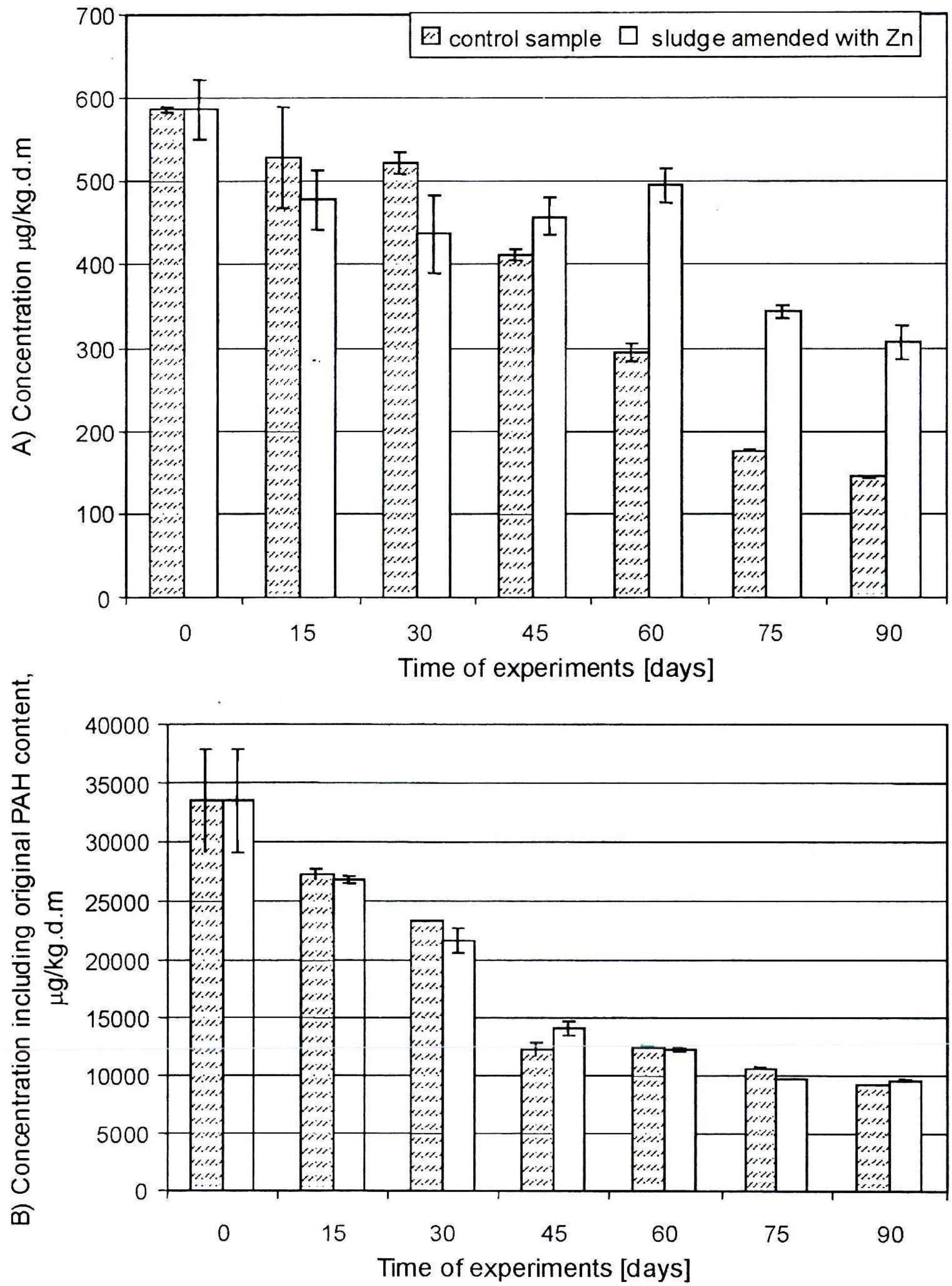


Fig. 3. Changes in 4-ring PAH concentrations in sewage sludge A) control sample, B) with standard mixture

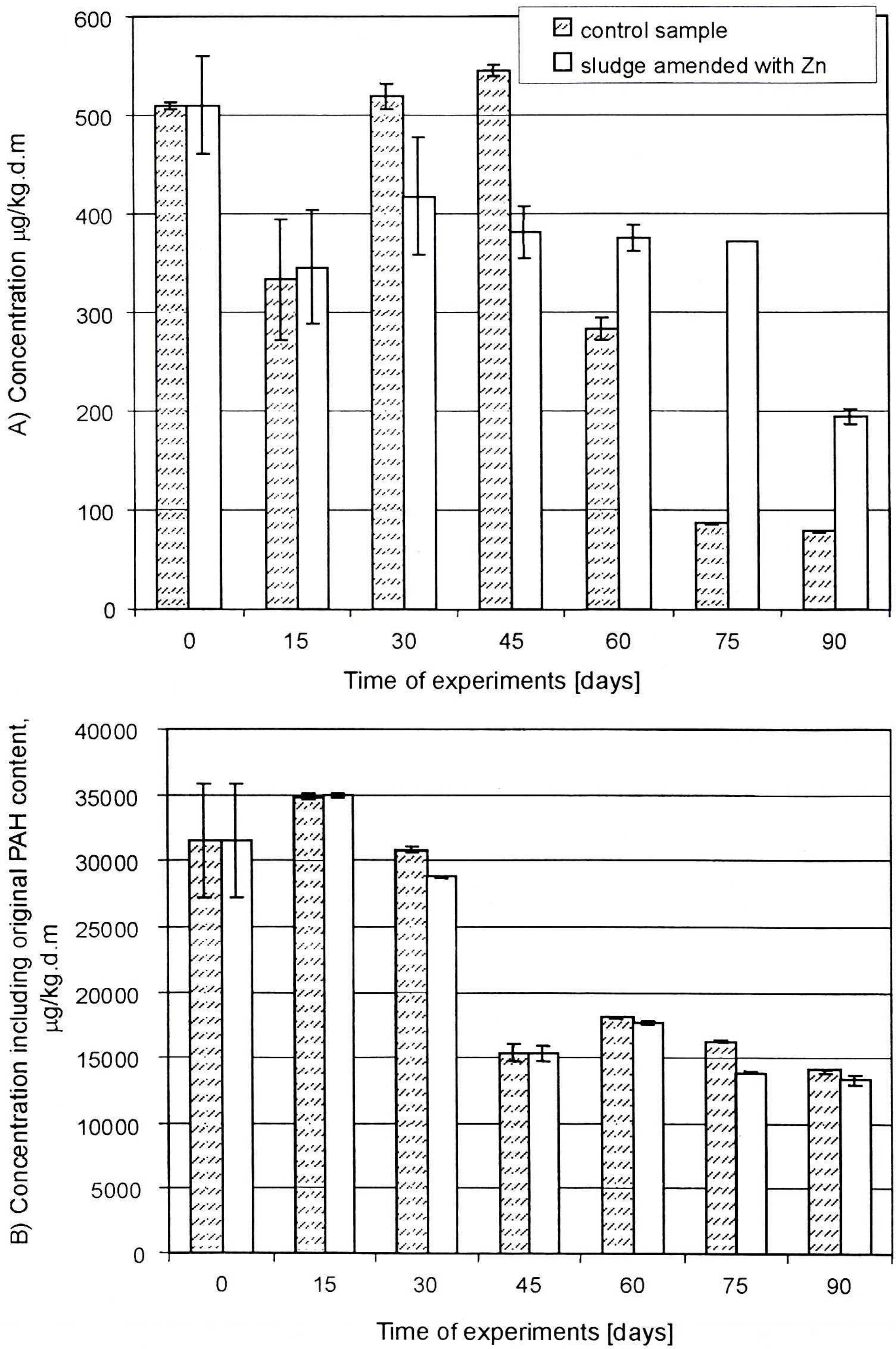


Fig. 4. Changes in 5-ring PAH concentrations in sewage sludge A) control sample, B) with standard mixture

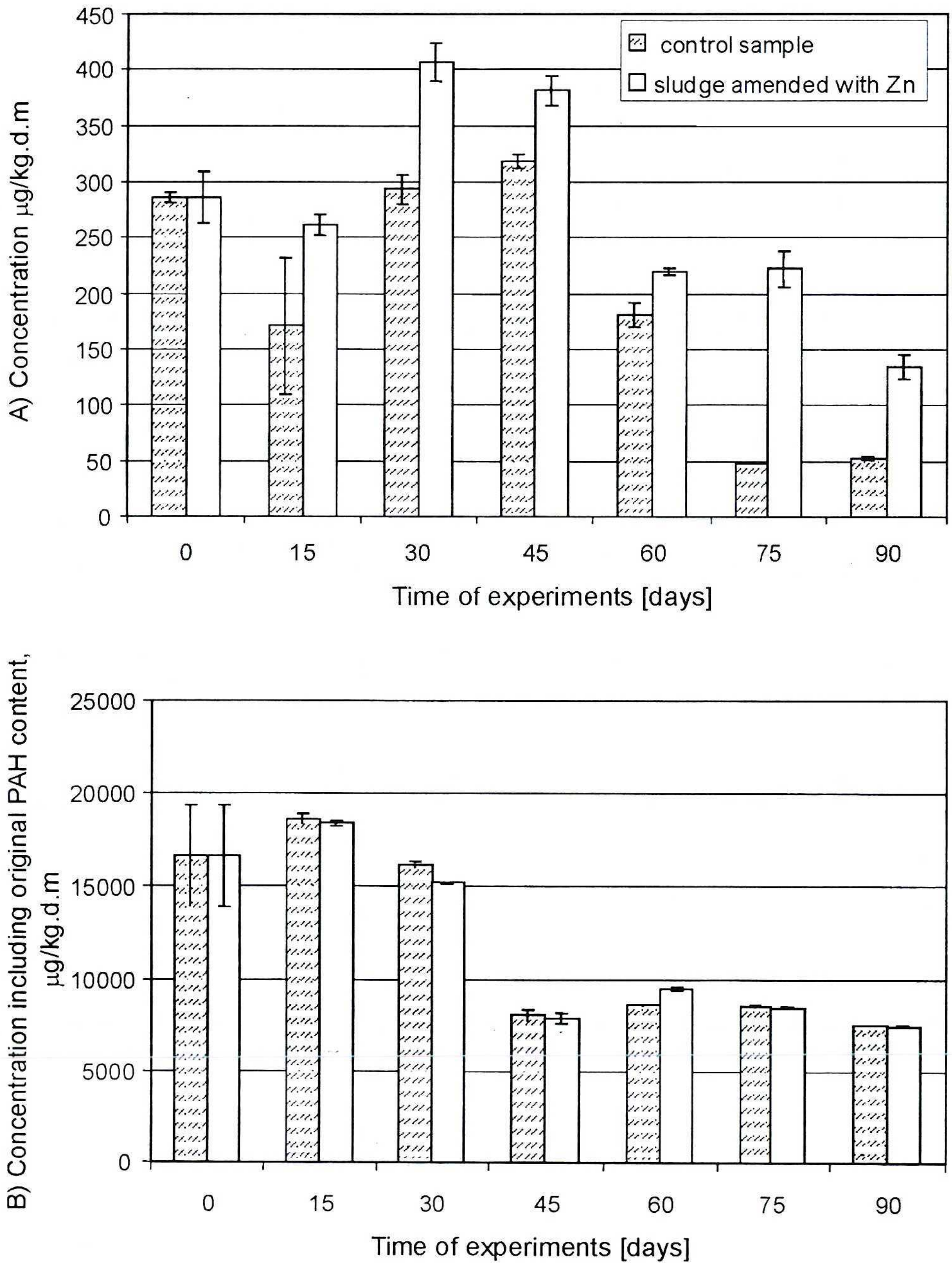


Fig. 5. Changes in 6-ring PAH concentrations in sewage sludge A) control sample, B) with standard mixture

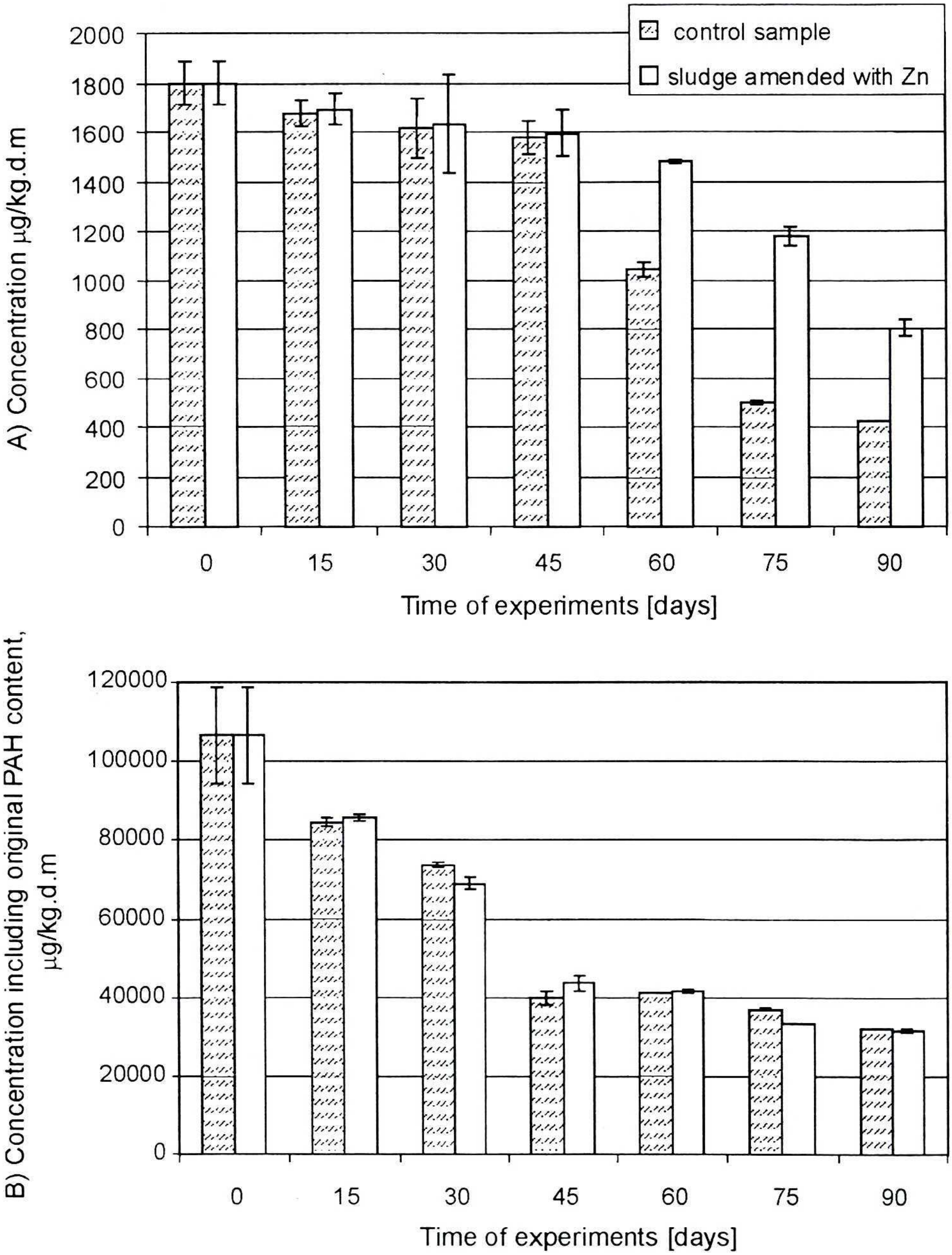


Fig. 6. Changes of 16 PAHs concentration in sewage sludge A) control sample, B) with standard mixture

A Student t-test was used in order to assess the statistically significant differences between the initial and final PAH concentrations as well as in order to estimate the statistically significant presence of Zn in sludges after 90 days of incubation [19]. It was estimated that changes in naphthalene concentrations and 5- and 6-ring hydrocarbons between the initial and final concentrations differed significantly in the control sludges and in sludges with zinc chloride added. Changes in 4-ring hydrocarbon concentrations differed significantly only in the control sludges (difference between the initial and final concentrations). The addition of zinc had a significant impact on changes in naphthalene concentrations and on 4-, 5- and 6-ring hydrocarbons (difference between control and sludge with Zn added).

Changes in concentrations of 3-ring hydrocarbons in samples taken before and after incubation were not significant. Significant differences were not found either in the control sample and in sample with Zn added.

The dynamics of hydrocarbon changes in sludges supplemented with the standard mixture with and without zinc chloride addition (B) are given in Figures 1–6. The initial PAHs concentration in sludges supported by the standard mixture was 106002 mg/kg d.m. The gradually lower concentration of PAHs was determined during the incubation of the samples irrespective of zinc occurrence. The differences in results between the total hydrocarbons determination in sludges with and without zinc added did not exceed 7%. Fluctuations in naphthalene concentration were also found. In the initial step of the investigation (after 15 days) a sharp decrease in naphthalene concentration by 96% in sludges without zinc and of 85% in sludges with zinc was observed which indicates volatilization losses. Within the further time intervals the average naphthalene concentrations varied from 80 to 224 mg/kg d.m. in sludges, and from 27 to 532 mg/kg d.m. in sludges with zinc. After 90 days of incubation naphthalene concentration in sludges with zinc added and the standard mixture was 2-times higher than in sample sludges without zinc. The concentration of the remaining hydrocarbons groups was at a similar level during the experiments for both sludges. The final 16 PAH concentration was 32013 mg/kg d.m. and 31657 mg/kg d.m., respectively (30% of initial contents). However, the decrease of 3-ring hydrocarbons was between 95–96%, whereas 4-ring hydrocarbons were 72%. The loss of higher rings hydrocarbons did not exceed 58% despite the fact that sorptive properties of these compounds are regarded as high (partition coefficient octanol/water log K_{ow} is above 7 [8]). The statistical analysis shows that there are significant differences in sludges augmented with the standard mixture between the initial and final concentration of naphthalene and 3- and 4-ring hydrocarbons in the control sludges and in the sludges with Zn added. There is a significant difference between the total contents of 16 PAHs before and after incubation. No significant differences between the total PAH contents in the control sludges and in sludges with Zn added were found.

In sludges without the standard mixture the presence of Zn had a significant impact on the studied hydrocarbons and on the changes in the total PAHs contents after 90 days of incubation. This might have been due to the selective limitation of microorganisms activity that causes decomposition of individual groups of these compounds. Moreover, the following phenomena: sorption onto particles, volatilization and the possibility of binding with chlorine and formation of PAHs-related compounds which were not analyzed, cannot be excluded.

In sludges supplemented with the standard mixture no significant differences were found between the total PAH contents in the sludges samples and in the samples with Zn added. Thus, it is suggested that investigations into the dynamics of changes of PAH concentration in sludges should be carried out without an additional amount of hydrocarbons.

The results are similar to the literature sources [8, 11] concerning the behavior of PAHs in soil contaminated with heavy metals as well as in the sewage sludge composting process. It is stated that the stability of individual hydrocarbons could vary and the dynamics of changes of concentrations during incubation of studied materials could be irregular.

CONCLUSION

Based on the results of the experiments it can be concluded that:

1. gradually lower concentrations of the 16 studied PAHs were determined during the 90-day incubation of the samples under oxygen conditions. At the same time periodically higher naphthalene concentrations were determined;
2. significant differences between initial concentrations and final concentrations for naphthalene, 4-, 5-, 6-ring PAHs in control samples and for naphthalene, 5- and 6-ring PAHs in sludges with Zn added were observed;
3. the inhibition of PAH degradation was found in sludges supplemented with zinc chloride (final average PAH concentration in modified sludges was 2-times higher than in the control sample);
4. the presence of Zn did not have a statistically significant impact on changes in 3-ring hydrocarbons. Statistically significant differences in changes to naphthalene and 4-, 5- and 6-ring hydrocarbons concentrations between control sludge and sludge amended with Zn were found.
5. the dynamics of hydrocarbon changes in sludges supplemented with the standard mixture was similar to those observed in the sludges both with and without zinc chloride addition. The presence of Zn did not have a statistically significant impact on the total 16 PAHs in sludges supplemented with the standard mixture.

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REFERENCES

[1] Conte P., A. Zena, G. Pilidis, A. Piccolo: *Increased retention of polycyclic aromatic hydrocarbons in soils induced by soil treatment with humic substances.* Environ. Pollution, **112**, 27–31 (2001).

[2] Dz. U. Nr 134, poz. 1140, *Rozporządzenie Ministra Środowiska z dnia 1 sierpnia 2002 r. w sprawie komunalnych osadów ściekowych.* 2002 (in Polish).

[3] Feilberg A., T. Nielsen: *Photodegradation of Nitro-PAHs in Viscous Organic Media Used as Models of Organic Aerosols.* Environ. Sci. Technol., **35**, 108–113 (2001).

[4] Janosz-Rajczyk M., L. Dąbrowska, J. Płoszaj: *The changes of heavy metals during methane fermentation of conditioned sewage sludge.* Engineering and Protection of Environment, **2**, 157–166 (2003) (in Polish).

[5] Kirk P.W., J.N. Lester: *The Rate of Polycyclic Aromatic Hydrocarbons during Sewage Sludge Digestion,* Environ. Technol., **12**, 13–20 (1990).

[6] Kornmuller A., U. Wiesmann: *Continuous ozonation of polycyclic aromatic hydrocarbons in oil/water-emulsions and biodegradation of oxidation products,* Wat. Sci. Tech., **4-5**, 107–114 (1999).

[7] Korte N.A.: *Guide for the technical evaluation of environmental data,* Technomic Publishing

Comp., Inc Lancaster USA 1999.

[8] Lazzari L., L. Sperni, P. Bertin, B. Pavoni: *Correlation between inorganic (heavy metals) and organic (PCBs and PAHs) micro pollutant concentrations during sewage sludge composting processes*, Chemosphere, **41**, 427–435 (2000).

[9] Liste H., M. Alexander: *Accumulation of phenanthrene and pyrene in rhizosphere soil*, Chemosphere, **40**, 11–14 (2000).

[10] Malicka M.: *Biotechnological methods of soil treatment on organic compounds*, Gas, Water and Sanitation Technique, **2**, 40–46 (1994) (in Polish).

[11] Maliszewska-Kordybach B., B. Smreczak: *Influence of Zn, Pb i Cd on persistence PAHs in soil*, Silesian University of Technology, Gliwice, 53 (1997) (in Polish).

[12] Maliszewska-Kordybach B.: *The effect of temperature on the rate of disappearance of polycyclic aromatic hydrocarbons from soils*, Environ. Pollution, **79**, 15–20 (1993).

[13] Means J.C., S. Wood, J. Hassett, L. Banwart: *Sorption of polynuclear aromatic hydrocarbons by sediments and soils*, Environ. Sci. Technol., **14**, 1524–1528 (1990).

[14] Perez S., M. Guillamon, D. Barcelo: *Quantitative analysis of Polycyclic Aromatic Hydrocarbons in Sewage Sludge from Wastewater Treatment Plants*, Journal of Chromatography, 938, 57–65 (2001).

[15] Rockne K.J., S.E. Strand: *Biodegradation of Bicyclic and Polycyclic Aromatic Hydrocarbons in anaerobic Enrichments*, Environ. Sci. Technol., **32**, 3962–3967 (1998).

[16] Stringfellow W.T., L. Alvarez-Cohen: *Evaluating the relationship between the sorption of PAHs to bacterial biomass and biodegradation*, Wat. Res., **11**, 2535–2544 (1999).

[17] Weber W., T. Young: *A distributed reactivity model for sorption by soils and sediments. 6. Mechanistic Implications of Desorption under Supercritical Fluid Conditions*, Environ. Sci. Technol., **31**, 1686–1691 (1997).

[18] Włodarczyk-Makuła M., E. Wiśniowska: *Changes of PAHs content during sewage sludge processing*, Fres. Environ. Bull., **10**, 936–940 (2004).

[19] Zgirski A., R. Gondko: *Obliczenia biochemiczne*, PWN, Warszawa 1998 (in Polish).

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