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HALF-LIFE OF CARCINOGENIC POLYCYCLIC AROMATIC  
HYDROCARBONS IN STORED SEWAGE SLUDGE

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**Keywords:** Sewage sludge, carcinogenic PAHs, half-life, exponential equation, deposition.

**Abstract:** In Poland, according to the statistical data, about 40% of sewage sludges originating from wastewater treatment plants are applied in the agriculture. The mentioned way of application of sewage sludges causes the hazard of contamination of environment with carcinogenic compounds due to the presence of some organic micropollutants, such as polycyclic aromatic hydrocarbons (PAHs). The proposal of changing UE Directive obligates control of organic pollutants (PAHs and others) in sewage sludges applied in the agriculture.

The aim of the investigations was to estimate the persistence of PAHs under stored conditions by determining half-life of their decomposition. Eight carcinogenic PAHs, among 16 compounds, listed by EPA were determined. In this study, the quantity changes in the concentration of PAHs in stored sewage sludges were investigated. Sewage sludges were stored under aerobic conditions for 16 weeks. At the same time the sewage sludges with sodium azide added, in order to deactivate the microorganisms (abiotic samples), were also stored. Gas chromatography-mass spectrometry was used to qualify and quantify PAHs in 2- and 4-week intervals. Sewage sludges were taken two fold from a municipal wastewater treatment plant. In practice, the sewage sludges are directed to the disposal site. The initial concentration of 16 PAHs in sewage sludge was equal to 582  $\mu\text{g}/\text{kg.d.m}$ . The changes in the concentration of PAHs corresponded to exponential function. Values of correlation coefficients indicate a significant dependence of PAHs persistence and concentration on time exposition. Under experimental conditions the half-lives of individual compounds were diversified. In biotic samples half-life of hydrocarbons was in the range of 17 to 126 days. Half-life of PAHs in abiotic sewage sludges was in the range of 32 to 2048 days. The most persistent were benzo(a)pyrene and benzo(b)fluoranthene, respectively. A significant dependence of PAHs' decrease on the presence of microorganisms in sewage sludges after 10 weeks of storage was found.

## INTRODUCTION

According to European legislation WE No 850/2004 based on Stockholm Convention 2001 polycyclic aromatic hydrocarbons (PAHs) belong to the group of persistent organic pollutants (POPs) [9]. They are also listed in the Frame Water Directive as one of priority pollutants of water environment [8]. PAHs may undergo the process of degradation under certain conditions. Effectiveness of the degradation

depends on the presence of proper microorganisms and on environmental conditions (temperature, water content, redox potential, pH, presence of oxygen) [2, 4, 10, 12, 24, 27]. In the wastewater treatment plant PAHs mainly adsorb onto solid particles (sewage sludge) [1, 3, 6, 11]. The presence of PAHs is also confirmed in raw sewage sludges as well as in digested sludge and dewatered sewage sludges [11, 16, 21]. Sewage sludges drained off from wastewater treatment plants can be used in the agriculture in order to improve soil conditions, for environmental purposes (e.g. reclamation of degraded areas) or stored [5]. Polish legislation limits environmental application of sewage sludges mainly due to the presence in them of selected heavy metals and pathogens. The proposed changes to the EU Directive on the use of sludge concern the introduction of permissible concentrations of polycyclic aromatic hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Polychlorinated Dibenzodioxins (PCDD), Polychlorinated Dibenzofurans (PCDF), Di-(2-ethylhexyl) phthalate (DEHP), Adsorbable organic halogens (AOX) and Linear Alkylbenzene sulfonate (LAS) in sewage sludges that can be applied in the agriculture [18, 25]. The presence of PAHs in sewage sludges results in a considerable load of PAHs entering into the environment [7, 14, 22, 25]. The load of sewage sludges with PAHs depends on the type of wastewater flowing into the wastewater treatment plant. The highest concentrations of PAHs were determined in sewage sludges originating from fuel processing industry (coke production and crude oil processing). In sewage sludges originating from municipal wastewater the concentration of PAHs depends on the type, amount and level of self-treatment of wastewater remaining after production processes with the PAH concentrations up to 80 mg/kg.d.m [8, 19, 20].

Stability of PAHs is defined as half-life of their decomposition. On the one hand there is a wide range of the literary sources with respect to PAHs and quite often the information of the persistence of these compounds can be found, but on the other hand only limited number of sources show determination of time of the decomposition. The available investigations take into account mainly soils or the mixture of soil and sewage sludges. It was found that half-lives of PAHs were in the range of 3 to 3111 days and of 15 to 408 days in the mixture of soil with sewage sludge and in soil, respectively [14, 17]. In the above mentioned investigations it was proved that persistence of PAHs depends on the structure and properties of individual compounds. Additionally, it depends on type and soil properties such as pH, temperature, the content of fulvic acids, humine and water, sorption capacity, and the presence of microorganisms able to decompose PAHs [2, 10, 12, 14, 17]. The results of investigations described in the literature are not always comparable because of the heterogeneity of materials, such as sewage sludge and their different properties. Additionally, often only individual hydrocarbons which are added in certain amounts are analysed in the studies. The aforementioned conditions are never found in the environment. In sewage sludges formed during the process of wastewater treatment PAHs are found as mixtures. Digested sludges are settled with mixed population of the microorganisms. In the process of sewage sludge hygienization the amount of PAHs decreases up to 95% however, the decomposition of organic substances occurs at the same time. It is stated in the literature that the process of liming can cause increase of persistence of some PAHs [14]. Therefore, introducing the inhibitor of biological activity into sewage sludges allows for comparing the level of PAHs decomposition under biotic and abiotic conditions.

The aim of the investigations was to compare the changes in the concentration of PAHs in stored sewage sludges both in the presence of microorganisms and without biological activity of the microorganisms. The stability of PAHs was described by calculating half-life of decomposition of hydrocarbons. The coefficients of determination and equations of curves trends of changes of PAHs concentration during the experiment were also calculated. The correlation coefficients between half-life of PAHs and concentration of the above mentioned compounds and correlation coefficients between PAHs concentration and time of their storage were determined. The significance of the presence of microorganisms in PAHs losses was also determined.

## MATERIALS AND METHODS

### *Materials*

The study was conducted with the use of sewage sludge collected from municipal wastewater treatment plant (the region of Silesia), to which household and industrial wastes are conveyed (30%) (population equivalent is higher than 100 000). Digested and dewatered sewage sludges used in this study were taken two fold. The treatment of sewage sludges is carried out under two-stage digestion and dewatering with the addition of organic polymer. Sewage sludges were primary analyzed by determining physical-chemical properties. The level of mineralization of organic compounds was determined by organic substrate matter content and water content in the sewage sludge as well as alkalinity and pH in the water extract. The analyses were performed according to the applied procedure [23]. The organic substrate matter content and water content was determined by weighing, whereas, pH and alkalinity were determined potentiometrically in water extracts. The concentration of Zn and Ni was also determined by ASA method. Before the experiment sewage sludges had low water content of 80% and low content of organic substrate matter (45%) on average. The pH was in the range of 7.5 to 7.8. Average alkalinity of water extract was equal to 4250 mg CaCO<sub>3</sub>/L. Physical-chemical properties of dewatered sewage sludge indicate that the sewage sludge was well digested. However, high concentration of Zn (2580 mg/kg.d.m) and Ni (130 mg/kg.d.m) makes the agricultural application of sewage sludge impossible.

### *Experimental procedure*

In order to perform the studies on the persistence of PAHs in sewage sludges the following samples were prepared:

- sewage sludge taken from dewatering system (biotic samples)
- sludge with sodium azide (NaN<sub>3</sub>) added in order to deactivate the microorganisms (abiotic samples) [15].

When double sampling 28 samples of 10 grams in 100 mL glass volumetric flasks were prepared each time. Sodium azide was added into 14 samples in the amount ensuring inhibition of microorganisms. The influence of added sodium azide on the activity of microorganisms was measured with the use of TTC test (dehydrogenase activity). In all samples with sodium azide added the dehydrogenase activity was equal to zero. Sewage sludges were kept under laboratory conditions without access to the light at 20°C for 16 weeks. The access to oxygen was not limited. The PAHs determination was carried

out 7 times: at the beginning of the experiment, after 2, 4, 6, 8, 10, 12 weeks of incubation and after 16 weeks, respectively. PAH extraction was performed with the entire volume of each sediment sample.

### **Calculation of PAHs half-life**

It was assumed that the speed of decomposition of substrate (PAHs) takes place according to the first-order reaction. Half-life  $T_{1/2}$  of hydrocarbons was calculated according to the following equations [14]:

$$T_{1/2} = \frac{\ln 2}{k} \quad \text{and} \quad \ln \frac{C_0}{C_t} = k \cdot t \quad (1)$$

$C_0$  – initial concentration of PAHs [ $\mu\text{g}/\text{kg.d.m}$ ],

$C_t$  – PAHs concentration in sewage sludge after  $t$  days of sewage sludge incubation [ $\mu\text{g}/\text{kg.d.m}$ ],

$t$  – time of incubation of sewage sludge [days],

$k$  – the reaction rate constant [ $\text{days}^{-1}$ ].

### **Statistical methods**

*Student t-test* was used for statistical evaluation of the results. A comparison of the efficiency of PAHs degradation in the presence of microorganisms and without microorganisms was conducted. The critical value was read from tables for specified degree of freedom ( $n-2$ ) and at a confidence level of 95%. Theoretical value of decomposition  $t_d$  was 4.303. Statistical calculations were done using *Statistica* programme.

### **PAHs analysis**

PAHs were determined using gas chromatography-mass spectrometry. Preparation of samples consisted in the extraction with the mixture of solvents: cyclohexane and chloromethane (in the ratio 5:1 (v/v)) [20, 21, 26]. The extraction process was carried out in ultrasonic bath. Then, the prepared extracts were concentrated under nitrogen stream and were purified using SPE columns packed with silica gel under vacuum conditions. Subsequently, the extracts were concentrated again and then analyzed using gas chromatography method. Qualitative and quantitative analysis was made using Fisons gas chromatograph (model CGC8000/MS800). The gas chromatographic separation was performed on DB-5 column (30-m length, 0.25 mm diameter and 1  $\mu\text{m}$  film). Helium was used as a carrier gas (the flow-rate of 0.5  $\text{mL min}^{-1}$ ). The oven was kept at 40°C for 1 min, heated with 5°C min to 120°C and a final temperature of 280°C was kept for 60 minutes. Eight carcinogenic PAHs were determined: benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene and indeno(123cd)pyrene [27]. In order to verify the applied procedure of preparation of sludge samples the recovery of standard mixture was also made. Standard mixture in the concentration of 3,000  $\mu\text{g}/\text{kg.d.m}$  was added to sewage sludge. Then, the samples were carefully shaken, extracted and analyzed for PAHs according to the procedure described above. Average PAHs recoveries from sewage sludge ranged from 67 to 104%. The recoveries obtained in the study correspond to the data found in the literature (0–128%) for complex organic matrices [11, 16, 21].

## RESULTS

The initial concentration of total eight PAHs in sewage sludge was equal to 582  $\mu\text{g}/\text{kg}$  d.m. The total content of eight hydrocarbons was ten times lower than permissible values of 11 compounds (6  $\text{mg}/\text{kg}$ .d.m) proposed in the Sludge Directive concerning the possibility of application of sewage sludges in the agriculture. However, in the investigations only five compounds (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(123cd)pyrene) among 16 analyzed are listed in the novel European regulations. The determined concentration is in the range of data found in the literature for sewage sludges originating from the European wastewater treatment plants, but it is a few times lower than the amount determined in the sewage sludges coming from the Asian wastewater treatment plants [18, 19]. The concentrations of individual compounds as well as the total concentration of 16 compounds determined in various sewage sludges differ significantly from each other. The characteristic of wastewater as well as methods and technological systems of wastewater and sewage sludges digestion processes have influence on PAHs concentration. In the investigations carried out by Oleszczuk the total concentration of 10 compounds in sewage sludges was in the range of 2,830–9,950  $\mu\text{g}/\text{kg}$  d.m [18]. Higher concentration of 13 PAHs was determined in sewage sludges coming from wastewater treatment plant in France with a ranging value of 16,200  $\mu\text{g}/\text{kg}$  d.m [3]. In the investigations provided by Oleszczuk 4-ring hydrocarbons were dominant, ranging from 50 to 67% of the 10 PAHs concentration, respectively [18]. In the abovementioned investigations the concentration of 5-ring hydrocarbons was the highest and these compounds amounted to 44% of the total contents of 8 PAHs (255  $\mu\text{g}/\text{kg}$  of dry mass).

The concentration of all hydrocarbons in the sewage sludge samples decreased during incubation of samples. The significantly lower concentration than the initial content of hydrocarbons was found after the first 2 and 4 weeks of sludge incubation. In the further period the decreases in the concentrations were lower. Due to the fact that determinations of PAHs were conducted in certain intervals, changes in the concentration were not presented as continuous function but trend lines of changes in the concentrations during the experiment were calculated as an exponential function. In Table 1 there are equations of curves of trends of changes in the PAHs concentration during incubation together with values of coefficient determination  $R^2$ . The value of coefficient  $R^2$  was in the range of 89 to 99%. This indicates that time of storage describes the value of concentration in 96% on average. Values of correlation coefficient show a significant negative dependence of half-life of PAHs and their concentration. The same negative correlation was also observed in the case of PAHs concentration and time of storage (Table 1).

Changes in the concentration of benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene in sewage sludges (both in biotic and abiotic samples) before incubation, after 2, 4, 6, 8, 10, 12 weeks and after 16 weeks are presented in Figure 1.

After 16 weeks of incubation the sum of concentration of these compounds was of 90% lower than the initial content (24  $\mu\text{g}/\text{kg}$ .d.m) in biotic sewage sludge. In sewage sludge with sodium azide added the removal (abiotic samples) of these compounds did not exceed 70  $\mu\text{g}/\text{kg}$ .d.m. The final concentration of these compounds was lower than the initial concentration by 78%. Changes in the concentration of benzo(a)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene and indeno(123cd)pyrene in sewage sludges are presented in Figure 2.

Table 1. The equations of curves of PAHs changes in sewage sludge (x – time of sewage sludge stored, y – concentration of PAHs), coefficient of determination and correlation coefficient

Compound	Biotic samples		Abiotic samples	
	correlation coefficient between		correlation coefficient between	
	Half-life of PAHs and their concentration	PAHs concentration and time of storage	Half-life of PAHs and their concentration	PAHs concentration and time of storage
	Equation of trends curve	Coefficient of determination	Equation of trends curve	Coefficient of determination
Benzo(a) anthracene	-0.882	-0.994	-0.883	-0.946
	$y=93.5e^{-0.382x}$	$R^2= 0.989$	$y=92.4e^{-0.342x}$	$R^2= 0.895$
Chrysene	-0.876	-0.945	-0.885	-0.967
	$y=94.5e^{-0.154x}$	$R^2= 0.894$	$y=91.3e^{-0.651x}$	$R^2= 0.935$
Benzo(b) fluoranthene	-0.905	-0.958	-0.918	-0.962
	$y=69.5e^{-0.721x}$	$R^2= 0.919$	$y=67.5e^{-0.421x}$	$R^2= 0.925$
Benzo(k) fluoranthene	-0.894	-0.961	-0.912	-0.955
	$y=61.5e^{-0.245x}$	$R^2= 0.923$	$y=59.2e^{-0.253x}$	$R^2= 0.912$
Benzo(a) pyrene	-0.944	-0.976	-0.960	-0.985
	$y=49.5e^{-0.652x}$	$R^2= 0.954$	$y=47.8e^{-0.205x}$	$R^2= 0.971$
Dibenzo(ah) anthracene	-0.904	-0.981	-0.904	-0.975
	$y=76.2e^{-0.245x}$	$R^2= 0.962$	$y=74.2e^{-0.301x}$	$R^2= 0.951$
Benzo(ghi) perylene	-0.917	-0.946	-0.922	-0.981
	$y=73.5e^{-0.352x}$	$R^2= 0.895$	$y=71.8e^{-0.254x}$	$R^2= 0.962$
Indeno(123, cd)pyrene	-0.918	-0.954	-0.924	-0.948
	$y=73.9e^{-0.452x}$	$R^2= 0.911$	$y=72.5e^{-0.403x}$	$R^2= 0.899$

The initial concentration of the aforementioned PAHs in sewage sludge was 270  $\mu\text{g}/\text{kg.d.m}$  on average. At the end of the experiment the total concentration of these compounds was lower than the initial concentration by 88% in biotic samples (30  $\mu\text{g}/\text{kg.d.m}$ ). In the sewage sludge samples with the inhibited activity of microorganisms the final total concentration of the four PAHs was equal to 52  $\text{g}/\text{kg.d.m}$ . and was lower than the initial content by 80%.

In Table 2 half-lives of hydrocarbons are given. Ranges of value of time decomposition were determined for various time intervals of sewage sludges storage (6 intervals). The half-life of benzo(b)fluoranthene corresponded to 126 days in biologically active sewage sludge samples and 164 days in abiotic sewage sludge samples, respectively. Due to the minor decrease of concentration in the initial period of the investigations, the time of the decomposition calculated based on the decrease had the highest value. The half-time of benzo(a)anthracene, chrysene and benzo(k)fluoranthene was in the range of 24 to 43 days. In abiotic sewage sludge samples the half-time was in the range of 46 to 123 days. In Table 2  $t_d$  values calculated for PAHs concentration in biotic and abiotic sewage sludges

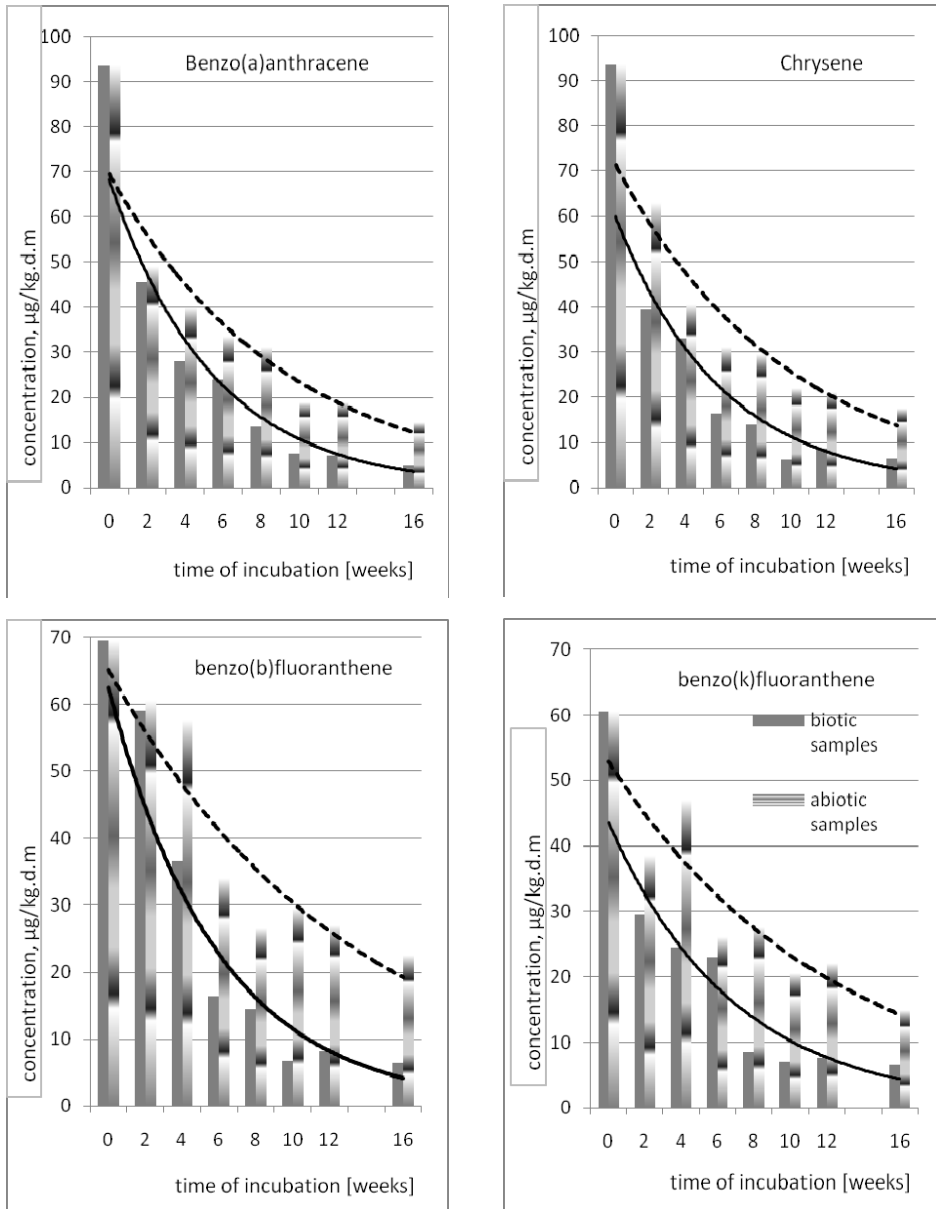


Fig. 1. Changes in the concentration of benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene in sewage sludges. Curves of trends of changes in the concentration of PAHs in biotic (solid line) and abiotic sewage sludges (broken line)

in set time intervals are presented. According to *Student t-test* the determined critical values  $t_d$  for hydrocarbon concentrations after 10, 12 and 16 weeks were in the range of 7.12 do 25.24. They were higher than the critical value equal to 4.303. That means that the presence of microorganisms was statistically significant in the removal of PAHs.

Table 2. Half-life of PAHs, Student test td value confidence changes in the concentration of PAHs in biotic and abiotic sewage sludges

PAH	Condition	Time of sewage sludge stored [week]						
		2	4	6	8	10	12	16
		Half-time of PAHs [days]						
Benzo(a) anthracene	Biotic	16	32	28	24	28	26	27
	Abiotic	52	47	37	41	37	44	39
	td value	1.31	2.02	8.50	3.29	<b>7.45</b>	<b>11.40</b>	<b>12.22</b>
Chrysene	Biotic	26	24	30	24	24	27	<b>35</b>
	Abiotic	37	53	38	45	43	55	44
	td value	4,23	2.79	1.78	4.47	<b>11.92</b>	<b>7.65</b>	<b>8.45</b>
Benzo(b) fluoranthene	Biotic	126	63	48	39	33	45	38
	Abiotic	164	159	95	88	73	54	59
	td value	0.47	8.24	3.48	4.12	<b>25.24</b>	<b>7.12</b>	<b>9.02</b>
Benzo(k) fluoranthene	Biotic	34	29	35	43	26	28	38
	Abiotic	23	46	123	49	66	57	52
	td value	1.75	20.12	0.51	4.45	<b>7.47</b>	<b>7.15</b>	<b>8.32</b>
Benzo(a) pyrene	Biotic	52	103	56	57	65	65	72
	Abiotic	1085	2048	62	88	83	79	99
	td value	2.22	0.73	3.61	4.54	<b>5.33</b>	<b>6.44</b>	<b>7.03</b>
Dibenzo(ah) anthracene	Biotic	18	27	18	23	22	25	30
	Abiotic	38	42	37	38	47	52	50
	td value	<b>5.53</b>	<b>8.88</b>	<b>6.93</b>	<b>4.44</b>	<b>8.69</b>	<b>22.78</b>	<b>28.28</b>
Benzo(ghi) perylene	Biotic	57	54	99	60	50	67	64
	Abiotic	50	100	105	61	52	71	75
	td value	1.17	0.15	0.12	0.39	0.32	0.63	3.67
Indeno(123 cd)pyrene	Biotic	32	23	34	39	31	29	37
	Abiotic	33	37	61	50	33	35	38
	td value	2.42	3.64	5.81	1.34	<b>5.66</b>	<b>4.41</b>	<b>3,03</b>
Total carcinogenic PAHs	Biotic	17	35	37	36	37	38	44
	Abiotic	28	37	39	43	44	61	68
	td value	2,92	4,17	4,24	2,53	<b>4,75</b>	<b>6,33</b>	<b>6,70</b>

According to the literature data, biodegradation of PAHs is possible but the primary adoption of the microorganisms is required [1, 12].

Benzo(a)pyrene was the most persistent hydrocarbon, its half-time was 103 days in biotic sewage sludge samples and 2,048 days and abiotic sewage sludge samples, respectively. After 10 weeks of incubation, td for benzo(a)pyrene was in the range



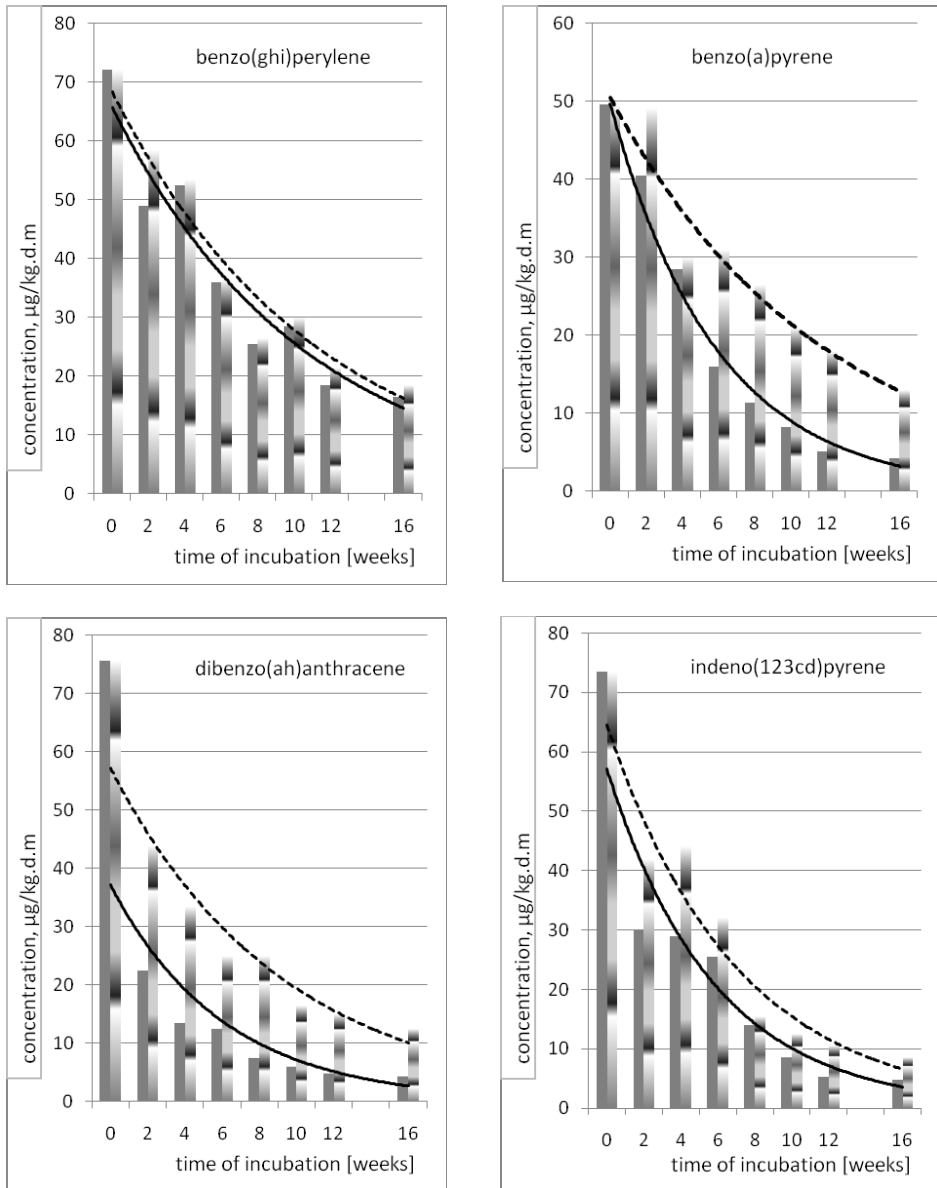


Fig. 2. Changes in the concentration of benzo(a)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene and indeno(123cd)pyrene in sewage sludges. Curves of trends of changes in the concentration of PAHs in biotic (solid line) and abiotic sewage sludges (broken line)

of 5.33 to 7.0 (Table 2). Therefore, after 10 weeks of sewage sludges incubation the biodegradation of the mentioned hydrocarbons is possible. Among investigated hydrocarbons, the highest life-time equal to 2,048 days was determined for benzo(a)pyrene in abiotic sewage sludge samples. On the other hand, much lower values in

the range of 52 to 100 days were obtained for biotic sewage sludges. The statistical calculations proved that the presence of microorganisms was statistically significant in the losses of dibenzo(ah)anthracene in the full period of sludges incubation because the critical value  $t_d$  was in the range of 5.53 to 28.28 (Table 2). The critical values of the test were in the range of 0.12 to 3.67 with the respect to benzo(ghi)perylene. The half-life of benzo(ghi)perylene was in the range of 50 to 105 days, respectively, and it was independent on the presence of microorganisms.

The abiotic losses might have been related to the reactions with other compounds of sewage sludges as well as to sorption, photodegradation, oxidation and evaporation [3, 14, 17]. The conditions of the experiment performed limited the process of photodegradation (incubation of samples without access to the light). The studied hydrocarbons have low values of Henry's constant, therefore, volatilization losses should also be considered insignificant. Due to the fact that the sewage sludge are a heterogeneous material with a complex organic and inorganic matrix, sorption could hinder the extraction and biodegradation of PAHs.

The obtained results are in the range of results obtained by other authors which were mentioned in the introduction. However, the comparison of the mentioned results is difficult due to the fact that in the literature half-time of those PAHs in soils, in the mixture of soils is often determined for those matrices after addition of a well-know amount of hydrocarbons. In addition, consideration should be given to diverse microflora of soils and sediments as well as heterogeneity of matrices and various conditions of investigations.

## CONCLUSIONS

The total concentration of eight carcinogenic PAHs was reduced by 88% in biotic sewage sludges, whereas the final concentration of PAHs was lower than initial content by 79% in the abiotic samples, respectively. This indicates the possibility of biodegradation of these compounds in sewage sludges during deposition with the exception of benzo(ghi)perylene. The presence of microflora was important in the degradation process mainly from the 10th week of sewage sludge incubation for studied hydrocarbons with the exception of dibenzo(ah)anthracene. The presence of microflora was statistically significant through the whole period of the investigations for the dibenzo(ah)anthracene.

The half-life of carcinogenic hydrocarbons estimated for assumed conditions of the experiment was equal to 126 and 2,048 days in biotic and abiotic sewage sludge samples, respectively. The highest half-life was found for benzo(a)pyrene and benzo(b)fluoranthene. This means that the agricultural application of sewage sludges causes long-term environmental pollution with these carcinogenic hydrocarbons. It is important from the point of view of the pollution of plants and migration into food-chain as well as water contamination during infiltration and drainage of rainfalls.

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#### CZAS POŁOWICZNEGO ROZPADU RAKOTWÓRCZYCH WIEOPIĘŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W SKŁADOWANYCH OSADACH ŚCIEKOWYCH

Z ogólnej ilości osadów ściekowych powstających w polskich oczyszczalniach, około 40% jest wykorzystywana przyrodniczo. Ze względu na obecność mikrozanieczyszczeń organicznych takich jak WWA, ten sposób zagospodarowania osadów stanowi zagrożenie zanieczyszczenia środowiska rakotwórczymi związkami. Zmiana Dyrektywy osadowej Unii Europejskiej przewiduje wprowadzenie dopuszczalnych stężeń organicznych mikrozanieczyszczeń, w tym WWA, dla osadów przeznaczonych do rolniczego wykorzystania. Celem badań była ocena trwałości WWA w warunkach składowania poprzez wyznaczenie czasu połowicznego rozpadu. Określono zmiany ilościowe WWA w osadach przechowywanych w warunkach tlenowych przez 16 tygodni. W tych samych warunkach pozostawały także osady, w których zahamowano aktywność mikroorganizmów poprzez dodatek azydru sodu. Ilościową analizę WWA prowadzono z wykorzystaniem zestawu GC-MS w odstępach 2, 4-tygodniowych równoległe w osadach biotycznych i abiotycznych. Oznaczano 8 rakotwórczych WWA (BaA, Ch, BbF, BkF, BaP, DahA, BghiP, IP), które znajdują się wśród 16 związków podanych na liście EPA. Osady pobrano dwukrotnie z oczyszczalni ścieków komunalnych, które w praktyce kierowane są na składowisko. Zawartość początkowa WWA w osadach była na poziomie 582  $\mu\text{g}/\text{kg.s.m}$ . Do opisu trendu zmian stężenia WWA w czasie składowania najodpowiedniejsza jest funkcja wykładnicza. Wartości współczynników korelacji wskazują na silną zależność trwałości WWA i stężenia od czasu składowania. W warunkach prowadzonego eksperymentu czas połowicznego rozkładu był zróżnicowany dla poszczególnych związków. W osadach aktywnych biologicznie czas połowicznego rozpadu badanych węglowodorów był w granicach od 17 do 126 dni. Czas połowicznego rozpadu wyznaczony dla WWA w osadach nieaktywnych biologicznie pozostawał w zakresie od 32 do 2048 dni. Najbardziej trwałe były: benzo(a)piren. i benzo(b)fluoranten. Stwierdzono istotną zależność ubytku WWA od obecności mikroorganizmów w osadach po 10 tygodniach składowania.