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STABILITY OF SELECTED PAHs IN SEWAGE SLUDGE

Maria WŁODARCZYK-MAKUŁA[1]
Czestochowa University of Technology,
Department of Chemistry, Water and Wastewater Technology, Poland

Abstract

The aim of the investigations was to estimate the half-life of selected PAHs in sewage sludge. Five hydrocarbons selected from 16 PAHs- EPA were chosen. In this study, the quantity changes in the concentration 3- and 4-ring of PAHs in sewage sludges were investigated. Sewage sludges were stored under aerobic conditions for 12 weeks. At the same time the sewage sludges with the added sodium azide, in order to deactivate the microorganisms (abiotic samples), were also stored. Gas chromatography-mass spectrometry was used to qualify and quantify PAHs in 2-week intervals. Sewage sludges were taken from a municipal wastewater treatment plant. Under experimental conditions the half-lives of individual compounds were diversed. In biotic samples half-life of hydrocarbons was in the range of 19 to 368 days. Half-life of PAHs in abiotic sewage sludges was in the range of 31 to 2961 days. The most persistent were phenanthrene.

Keywords: fluorene, phenanthrene, anthracene, fluoranthene, pyrene, half-live, sewage sludge, aerobic conditions, sodium azide

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) belong to the group of persistent organic pollutants (POPs) [6]. PAHs may undergo the process of degradation under certain conditions. Effectiveness of the degradation depends on the presence of proper microorganisms and environmental conditions [3,7,9,18]. In the wastewater treatment plant PAHs mainly absorb onto solid particles and accumulate in sewage sludge [1,2,4,8]. Sewage sludges can be used in the

[1] Corresponding author: Czestochowa University of Technology, 69 Dabrowskiego Str. 42-200 Czestochowa, e-mail: mwm@is.pcz.czest.pl, tel.+48343250919

agriculture in order to: improve soil conditions, for environmental purposes or stored. Polish legislation limits environmental application of sewage sludges mainly due to the fact of listing permissible concentration of seven metals and pathogens. The proposal of changing EU Directive with respect to sewage sludge gives permissible concentrations of PAHs, PCBs, PCDD/PCDF, DEHP, AOX and LAS in sewage sludges that can be applied in the agriculture [14]. The load of sewage sludges with PAHs depends on the type of wastewater flowing into the wastewater treatment plant (domestic, industrial) [15,16]. 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 mixture of soil with sewage sludge and in soil, respectively [10,13]. 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, content of fulvic acids, humine and water, sorption capacity, the presence of microorganisms able to decompose PAHs [7,9,10,13]. The results of investigations described in the literature are not unambiguous and heterogeneity of sewage sludge makes difficulties in comparison with the results. Additionally, often only individual hydrocarbons which are added in certain amounts are analysed in the studies. The afore mentioned conditions are never found in the environment. In sewage sludges forming 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 hygienization of sewage sludges the amount of PAHs decreases of 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 [10]. Therefore, introducing the inhibitor of biological activity into sewage sludges allows 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 the hydrocarbons.

2. MATERIALS AND METHODS

2.1. Materials

The experiments were carried out using sewage sludges originating from a municipal treatment plant to those the domestic and industrial wastewater (30%) flows in. Digested and dewatered sewage sludges were used in this study. Sewage sludges were primary analyzed by determining physical-chemical properties. Level of mineralization of organic compounds was followed by determining organic substrate matter content and water content in the sewage sludge. Organic substrate matter content and water content was determined by weighing. Before experiment sewage sludges had low water content of 81% and low content of organic substrate matter (44%) in average. The pH of sewage sludge was in the range of 7.5 to 7.8.

2.2. Experimental procedure

In the investigations into the persistence of PAHs in sewage sludges the following samples were prepared:

- dewatering sewage sludge taken from wastewater treatment plant (biotic samples)
- sewage sludge (described above) with added sodium azide (NaN_3) ($0.1 g/g_{.d.m}$) in order to deactivate the microorganisms (abiotic samples) [11].

Sewage sludges were kept under laboratory conditions without access to the light at 20° C for 12 weeks. The access to the oxygen was not limited. The PAHs determination was carried out 7 times: at the beginning of experiment, after 2, 4, 6, 8, 10, 12 weeks of incubation. PAHs were determined in duplicates by sacrificing the whole sample into the extraction. Student t-test was used in order to assess the statistically significance of the results. Comparison of affectivities of PAHs degradation in the presence of microorganisms and without microorganisms was calculated according to t-*Student* test. 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 td ranged 4,3.

2.3. Calculation of PAHs half-life

Assuming that 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 [10]:

$$T_{1/2} = \frac{\ln 2}{k} \quad \text{and} \quad \ln \frac{C_0}{C_t} = k \cdot t \qquad (1.1)$$

C_0 - initial concentration of PAHs [µg/kg.d.m]
C_t - PAHs concentration in sewage sludge after t days of sewage sludge incubation [µg/kg.d.m]
t - time of incubation of sewage sludge [days]
k - the reaction rate constant [days^{-1}]

2.4. PAHs analysis

PAHs were determined using gas chromatography - mass spectrometry. Preparation of samples consisted of the extraction by the mixture of solvents cyclohexane and chloromethane mixture (in the ratio 5: 1 (v/v)) [16,17]. The extraction process was carried out in ultrasonic bath. Then, prepared extracts were concentrated under nitrogen stream and were purified using SPE columns packed with silica gel under vacuum conditions. Subsequently, 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 µm film). Helium was used as a carrier gas (the flow-rate of 0.5 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. Five PAHs were determined: fluorene, phenanthrene, anthracene, fluoranthene and pyrene. In order to verify the applied procedure of preparation of sludge samples the recovery of standard mixture was also made. Then, the samples were analyzed for PAHs according to procedure described above. Average PAHs recoveries from sewage sludge ranged from 74 to 109%. The recoveries obtained in the study correspond to the data found in the literature (0-128%) for complex organic matrixes [8,12,17].

3. RESULTS AND DISCUSSION

The initial concentration of total 5 PAHs in sewage sludge was equal to 346µg/kg d.m. The determined concentration is few times lower than the amount determined in the sewage sludges coming from other wastewater treatment plants [2,14,15]. The concentration of all hydrocarbons in the sewage sludge samples decreased during incubation of samples. Changes in the concentration of 3-ring of PAHs (fluorine, phenanthrene, anthracene) in sewage sludges (both in biotic and abiotic samples) before incubation, after 2, 4, 6, 8, 10, 12 weeks are presented in Figure 1. Before incubation, the concentration of 3-ring of PAHs was equal 99µg/kg.d.m. After 12 weeks of incubation the sum of concentration of these compounds was of 62% lower than initial content (69µg/kg.d.m) in biotic sewage sludge. In sewage sludge with added sodium azide the removal (abiotic samples) of these compounds did not exceed 41µg/kg.d.m.

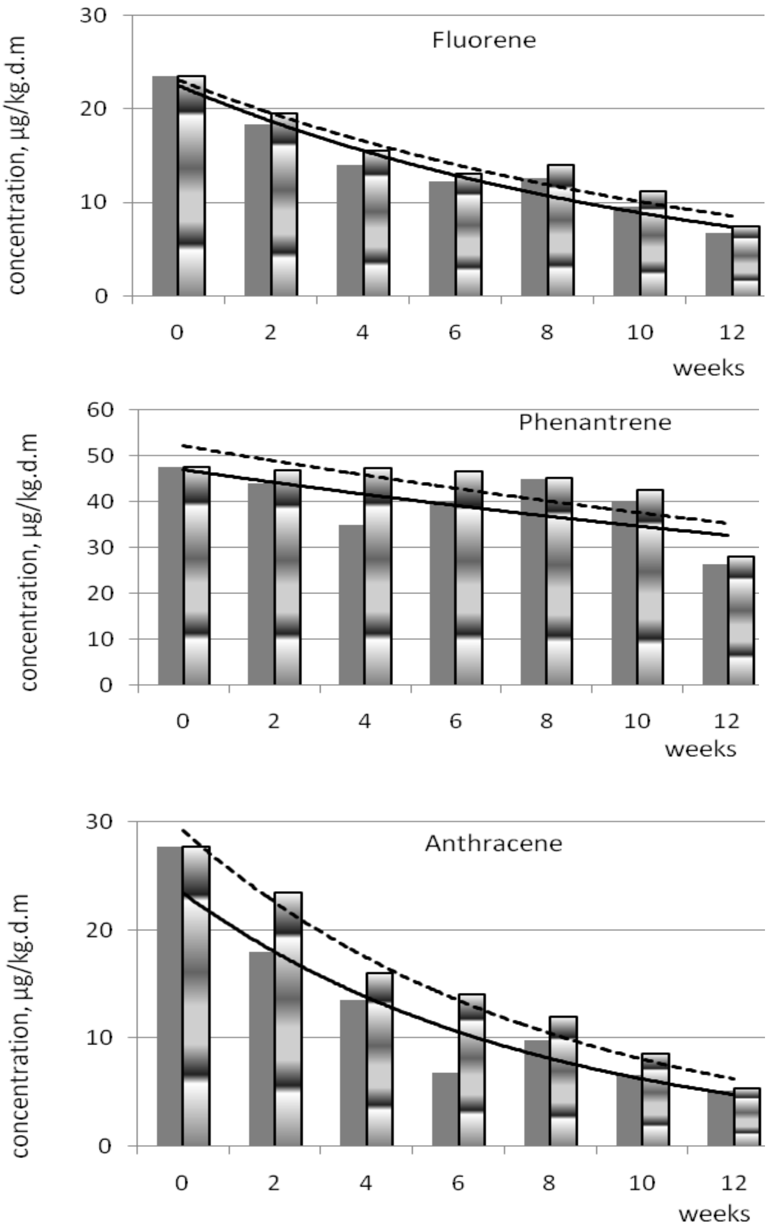

Fig. 1. Changes in the concentration of 3-ring of PAHs in sewage sludges. Curves of trends of changes in the concentration of PAHs in biotic (solid line) and abiotic sewage sludges (broken line)

The final concentration of these compounds was lower than initial concentration of 59%. Changes in the concentration of fluoranthene and pyrene (4-ring of hydrocarbons) in sewage sludges are presented in Figure 2. The initial concentration of the afore mentioned PAHs in sewage sludge was 247µg/kg.d.m on average. At the end of the experiment the total concentration of these compounds was lower than initial concentration of 87% in biotic samples (31 mg/kg.d.m). In the sewage sludge samples with the inhibited activity of microorganisms the final total concentration of fourth PAHs was equal to 92 µg/kg.d.m. and was lower than the initial content of 63%.

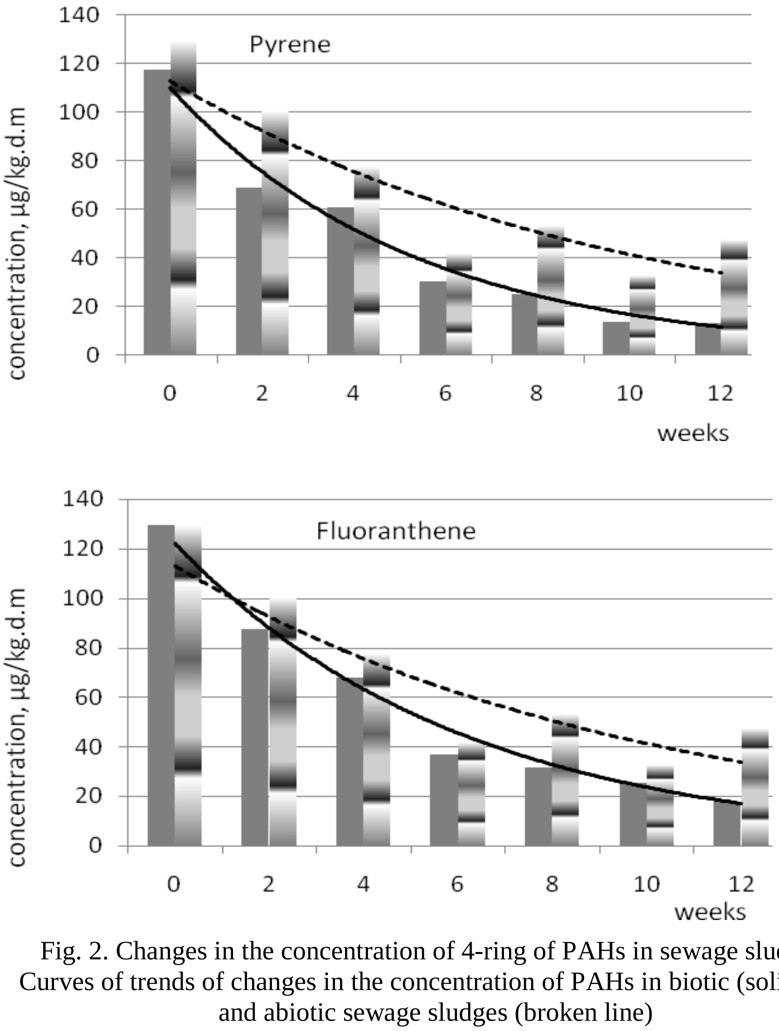

Fig. 2. Changes in the concentration of 4-ring of PAHs in sewage sludges.
Curves of trends of changes in the concentration of PAHs in biotic (solid line) and abiotic sewage sludges (broken line)

In Table 1 removal of hydrocarbons in sewage sludge (biotic and abiotic samples are given. In Table 2 half-lives of hydrocarbons are presented. Ranges of value of time decomposition were determined for various time intervals of sewage sludges storage (6 intervals).

Table 1. Removal of hydrocarbons [%] in sewage sludge (biotic and abiotic samples are given.

PAH	Condition	Time of sewage sludge stored [week]					
		2	4	6	8	10	12
3-ring of PAHs	Biotic	19	36	40	32	43	62
	Abiotic	9	20	25	28	37	59
4-ring of PAHs	Biotic	37	48	72	77	84	87
	Abiotic	25	43	70	61	76	63
Total of five PAHs	Biotic	32	45	63	64	72	80
	Abiotic	20	36	58	52	65	61

Table 2. Half-life of PAHs, *Student* test t_d 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
		Half-time of PAHs [days]					
Fluorene	Biotic	42	84	60	63	83	69
	Abiotic	55	111	75	71	100	84
	t_d value	0.48	0.73	0.33	0.61	2.18	0.83
Phenanthrene	Biotic	135	271	102	251	961	368
	Abiotic	892	1785	2961	2174	1024	579
	t_d value	0.82	2.14	0.75	0.03	0.36	1.5
Anthracene	Biotic	24	48	43	29	50	43
	Abiotic	63	125	57	61	62	53
	t_d value	3.05	1.21	3.76	1.07	1.16	0.17
Fluoranthene	Biotic	26	53	48	33	37	38
	Abiotic	41	82	61	37	58	45
	t_d value	1.51	2.27	2.66	**5.03**	**9.9**	**5.43**
Pyrene	Biotic	19	39	48	31	34	29
	Abiotic	32	64	51	31	52	42
	t_d value	2.74	1.67	2.62	**4.31**	4.11	**6.54**

The half-life of fluorene corresponded to 84 days in biologically active sewage sludge samples and 111 days in abiotic sewage sludge samples, respectively. Phenanthrene was the most persistent hydrocarbons. The half-time of phenenthrene was in the range of 102 to 961 days in biotic samples of sewage sludge. In abiotic sewage sludge samples the half-time was in the range of 579 to

2961 days. The half-life of anthracene was in the range of 24 to 50 days and in the range of 53 to 125 days in biotic and abiotic samples, respectively. The half-life of 4-ring of hydrocarbons was in the range of 19 to 53 days and in the range of 31 to 82 days in biotic and abiotic samples, respectively. Changes in concentration of these compounds was dependent of the presence of the microorganisms. According to statistic test the determined critical values td for 4-ring of PAHs concentrations were higher than the critical value equal to 4.3 after 8 weeks of incubation of sewage sludge. That means that the presence of microorganisms was statistically significant in the removal of these hydrocarbons. According to literature data, biodegradation of PAHs is possible but the primary adoption of the microorganisms is required [1,9]. The abiotic losses may be related to the reactions with other compounds of sewage sludges as well as sorption, photodegradation, oxidation and evaporation [2,5,10,13]. The conditions of the carried out experiment limited the process of photodegradation (incubation of samples without access to the light). The studied hydrocarbons have low values of Henry's constant therefore, vaporization should be out of concern in losses of these compounds. Sorption has of higher importance as it disturbs the processes of extraction and biodegradation, sewage sludges are heterogenic material consisting of complex organic and inorganic matrix. 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 matrixes after addition of well-know amount of hydrocarbons. It should also be pointed out the variety of microflora of soils and sewage sludges as well as heterogeneity of matrixes and various conditions of carrying investigations.

4. CONCLUSIONS

The total concentration of 3- and 4-ring of PAHs was reduced by 80% in biotic sewage sludges, whereas the final concentration of PAHs was lower than initial content of 61% in the abiotic samples, respectively. It indicates the possibility of biodegradation of these compounds in sewage sludges during deposition with the exception of phenanthrene. The presence of microflora was important in the degradation process mainly from the 12th week of sewage sludge incubation for studied hydrocarbons with the exception of phenanthrene. The half-life of investigated hydrocarbons estimated for assumed conditions of the experiment was equal to 19 - 369 and to 31 - 2961 days in biotic and abiotic sewage sludge samples, respectively. The highest half-life was found for phenanthrene. This means that the agricultural application of sewage sludges causes long-term environmental pollution with these 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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STABILNOŚĆ WYBRANYCH WWA W OSADACH ŚCIEKOWYCH

S t r e s z c z e n i e

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 12 tygodni. W tych samych warunkach pozostawały także osady, w których zahamowano aktywność mikroorganizmów poprzez dodatek azydku sodu. Ilościową analizę WWA prowadzono z wykorzystaniem zestawu GC-MS w odstępach 2-tygodniowych równolegle w osadach biotycznych i abiotycznych. Oznaczano pięć WWA (fluoren, fenentren, antracen, fluoranten, piren), 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 346µg/kg.s.m. 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 19 do 368 dób. Czas połowicznego rozpadu wyznaczony dla WWA w osadach nieaktywnych biologicznie pozostawał w zakresie od 31 do 2961 dób.

Słowa kluczowe: fluoren, fenantren, antracen, fluoranten, piren, czas półrozpadu, osady ściekowe, warunki tlenowe, azydek sodu

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