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Original Research Article

BIOTIC AND ABIOTIC DECOMPOSITION OF INDENO-PYRENE AND BENZO(GHI)PERYLENE IN SEWAGE SLUDGE UNDER VARIOUS LIGHT CONDITIONS

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A b s t r a c t

The aim of the studies was to determine the changes in the concentration of PAHs in sewage sludge stored under various light conditions. The sewage sludge samples were stored under aerobic conditions. Sewage sludge samples were deposed in darkness, in laboratory conditions and exposed to UV rays. The changes in the concentration of PAHs were analyzed in fourth series: in sludge samples taken from treatment plant (biotic samples), in sludge with the addition of a standard PAH mixture (biotic samples+PAHs), in sewage sludge with addition sodium azide (abiotic samples) and both a standard mixture and with added sodium azide (abiotic samples+PAHs). Changes in 6-ring of PAHs concentration in sewage sludge samples were studied at seven day intervals for 4 weeks. The concentration of PAHs was determination using gas chromatograph-mass spectrometry GC-MS. The losses of hydrocarbons after 4 weeks of research were in the range of 60 to 97%. It depends of kind of samples. In sewage sludge with standard mixture the effectiveness of PAHs decomposition were in the range of 60 to75%. In sewage sludge with standard mixture of PAHs the losses of hydrocarbons were the highest and reached 97%. The final concentration of PAHs in biotic samples was lower (2-13%) than the concentration of analysed compounds in abiotic samples.

Keywords: sewage sludge, PAHs, GC-MS, darkness, daily light, UV rays

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1. INTRODUCTION

In many countries sewage sludges originating from municipal treatment plants are applied in the agriculture. Sewage sludges support the structure of soil and enrich it with microcompounds. However, the presence of toxic organic micropollutants (PAHs, PCBs, AOX), in sewage sludges should also be taken into account [1-3]. The Polish legislation demands control of eight heavy metals as well as pathogen organisms only in sewage sludges to be applied in the agriculture [4]. PAHs are persistent compounds but under certain conditions they may undergo dcomposition under physical-chemical and biological factors and as a consequence they may form new chemical compounds [5-7]. The sewage sludges applied in agriculture are exposed to the changing environmental conditions. The level of decomposition depends on physical-chemical hydrocarbon properties, environment (water, soil, air) and environmental conditions (humidity, temperature, light, pH value) [8-10]. The changes in the concentration of PAHs in sewage sludges stored under various temperatures are presented earlier. [11]. Adsorption onto organic matter particles, biodegradation and, at a lower level, volatilization are regarded as the processes responsible for the changes in PAHs concentration during composting. [12]. The processes of PAHs decomposition are mainly related to chemical oxidation, volatilization and photodegradation. Photodegradation is one of the dominant processes of PAHs degradation in water environment. The mechanisms pathways of photolysis consist of the absorption of light by hydrocarbons and return to the ground form or being transformed into a radical cation [13-15]. In the literature there is rather scare information regarding the mechanism of photodegradation in sewage sludge in the agriculture applied. Furthermore, the described experiments were carried out using pure matrices (water, soil) to which one aromatic compound is usually added treated as the indicator of the whole group of polyaromatic hydrocarbons. Therefore, it is important to determine whether the susceptibility of PAHs on UV radiation is identical for the matrix containing other organic compounds as well as in the case of adding additional amount of PAHs (as a standard mixture). Stability of PAHs is defined as half-life of their decomposition [16-18]. 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- 3111 days in the mixture of soil with sewage sludge and from 15 to 408 days in soil, respectively [16]. In the earlier investigation, in biotic samples the half-time of low molecule weight hydrocarbons was in the range of 5 to 953 days. The most persistence were the hydrocarbons in sewage sludge stored without light conditions. The half- live of hydrocarbons content in sewage sludge amended with the standard mixture was lower in biotic samples than in abiotic samples for samples stored in darkness

and daily light conditions. In the samples exposed to UV rays the half-live of hydrocarbons was lower in abiotic samples than in biotic samples (in sewage sludge amended with the standard mixture) [17,18].
The aim of this investigation was to determine the changes of indeno(1,2,3cd)pyrene IP and benzo(ghi)perylene BghiP concentration in sewage sludge deposed under various light conditions. The objective of this research was to find out what impact various light conditions had on indeno(1,2,3 cd)pyrene and on benzo(ghi)perylene persistence in sewage sludges stored under aerobic conditions with standard mixture of PAHs and without standard mixture of PAHs. Pararelly the changes in concentration of PAHs in abiotic sewage sludge (with sodium azide) were studied (with standard mixture of PAHs and without standard mixture of PAHs).

2. MATERIALS AND METHODS

In the studies sewage sludges originating from a municipal treatment plant were used. The sludges had a low water content (78%) due to the dewatered sludges formerly biochemically stabilised. The organic matter content of 49% proved that the sludge was well digested. At the begging of the experiment (day 0) PAHs were determined in sewage sludge samples to be treated as the initial concentration. Sludge samples were homogenised to obtain a representative sample. 48 sewage sludge samples of 10 g each were prepared. The sodium azide was added to twenty four samples to inhibit microbial activity (abiotic samples). A standard mixture of PAH (concentration of 2000 μg/mL of each hydrocarbons) was added to 24 samples (12 biotic and 12 abiotic ones). All samples were incubated for four weeks at a temperature of 20°C in laboratory conditions under various light conditions. Sixteen sewage sludge samples were stored in the dark (without access to the light). The further sixteen sewage sludge samples were kept under access of natural day light conditions. The remaining 16 sewage sludge samples were stored in laboratory conditions and exposed to UV rays for four hours per day. The whole volume of each sludge sample was used sacrificed to determine PAHs. PAH samples were taken at the beginning of the experiment (the initial concentration) and three times at one week interval (after 1, 2, 3 and 4 weeks). The following investigations were made:

- assessment of the changes in IP and BghiP concentration in sewage sludge samples taken from municipal treatment plant (biotic samples),
- determination of the changes in IP and BghiP concentration in sewage sludge samples taken from a municipal treatment plant amended with a standard mixture of these compounds (biotic samples+PAHs),

- assessment of the changes in IP and BghiP concentration in sewage sludge samples supported sodium azide (abiotic samples),
- determination of the changes in PAH concentration in sewage sludge samples supported the standard mixture of these compounds as well as sodium azide (abiotic samples+PAHs).

The concentration of indeno(1,2,3cd)pyrene IP and benzo(ghi)perylene B(ghi)P in sewage sludge samples stored under different light conditions were made. The extraction of the mixture of solvents cyclohexane/dichloromethane was used in order to separate organic matrix from sludges (v/v 5/1). The extraction process using ultrasonic batch was carried out. The extracts were separated from sewage sludge samples in the centrifugation process. Prepared extracts were primarily concentrated under the nitrogen stream. Then extracts were purified on silica gel under vacuum conditions. Afterwards, the extracts were concentrated to the volume of 1 mL under nitrogen stream and analyzed using gas chromatograph and mass spectrometer (GC-MS).

3. RESULTS AND DISCUSSION

In the sludge samples taken from a treatment plant the initial concentration of indeno(1,2,3cd)pyrene and benzo(ghi)perylene ranged 61µg/kg of dry matter. The changes in the concentration of indeno-pyrene IP and benzo(ghi)perylene BghiP in the biotic and abiotic samples of sewage sludge during four weeks of incubation in darkness are given in Figures 1-2, respectively.

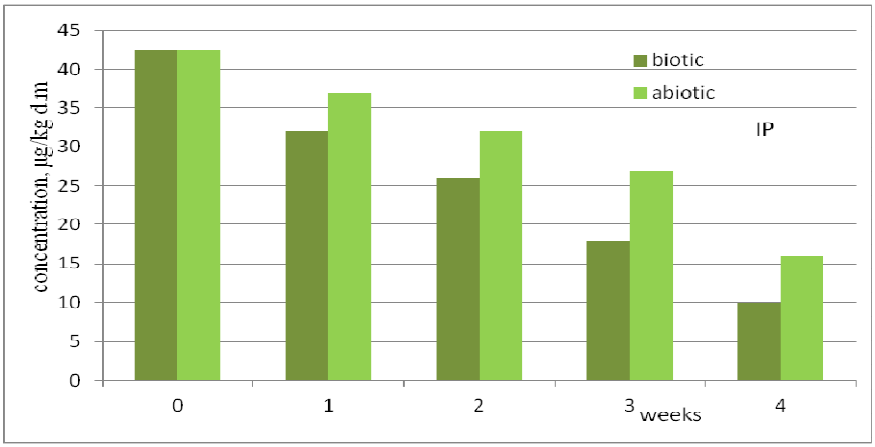

Fig. 1. Changes in the concentration of IP in sewage sludge (biotic and abiotic samples) during four weeks of incubation in darkness

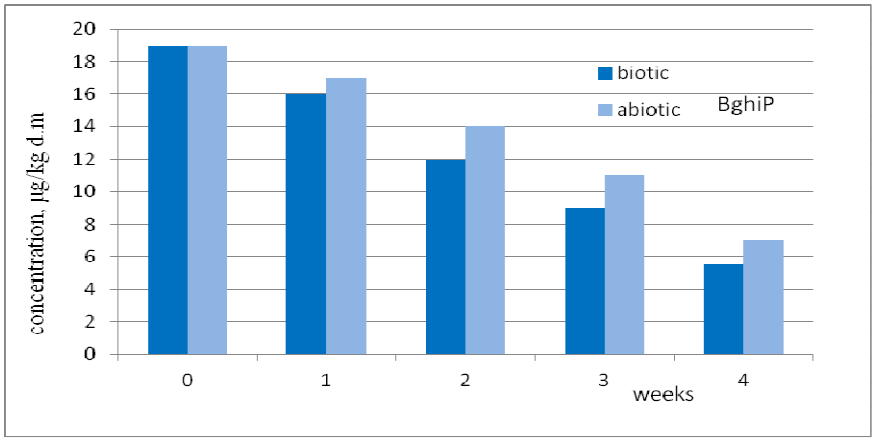

Fig. 2. Changes in the concentration of BghiP in sewage sludge (biotic and abiotic samples) during four weeks of incubation in darkness

After 4 weeks the total 6-ring of PAHs concentration was lower than in the initial ones of 75% and 62% in biotic and abiotic samples, respectively. The looses of hydrocarbons in abiotic conditions were lower than in presence of microorganisms. The changes in the concentration of IP and BghiP in the biotic and abiotic sewage sludge spiked with standard mixture are presented in Figures 3 and 4, respectively.

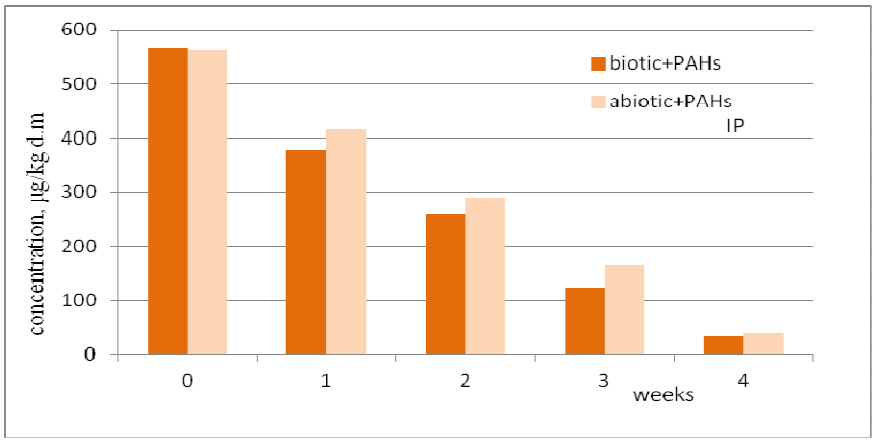

Fig. 3. Changes in the concentration of IP in sewage sludge (biotic and abiotic samples) amended with standard mixture during four weeks of incubation in darkness

The concentration of 6-ring of PAHs in sewage sludge spiked with standard mixture reached 1317 µg/kg.d.m. and 1308µg/kg.d.m in biotic and abiotic

samples, respectively. In sludge samples incubated in darkness after 4 weeks of the experiment the total contents of 6-ring of PAHs was lower than the initial concentration. In the sewage sludge the losses of these hydrocarbons and ranged 95% and 94% in biotic and abiotic samples, respectively. The dynamic of concentration changes of individual hydrocarbon in samples were similar in the samples. The highest looses of hydrocarbons were in the first week of incubation.

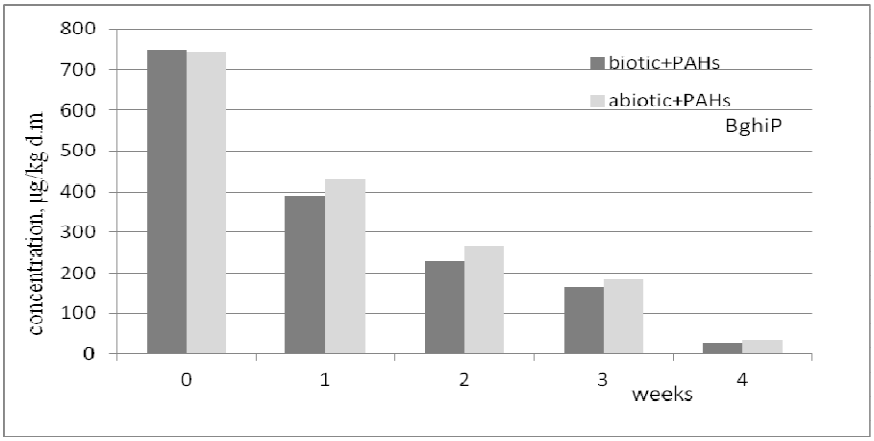

Fig.4. Changes in the concentration of BghiP in sewage sludge (biotic and abiotic samples) amended with standard mixture during four weeks of incubation in darkness

Changes in 6-ring hydrocarbons concentrations between the initial and final concentration were significantly in the all sewage sludges. The statistical analysis shows that there are significant differences in sludges augmented with the standard mixture among the concentration of hydrocarbons in the both sludges (without and with sodium azide) during deposed of sewage sludges. Changes in 6-ring hydrocarbons concentrations between the concentration of PAHs in biotic and abiotic samples were no statistically significantly.

In Figures 5 and 6 the changes in the concentration of analyzed hydrocarbons in sewage sludge (biotic and abiotic samples) stored under light conditions are presented.

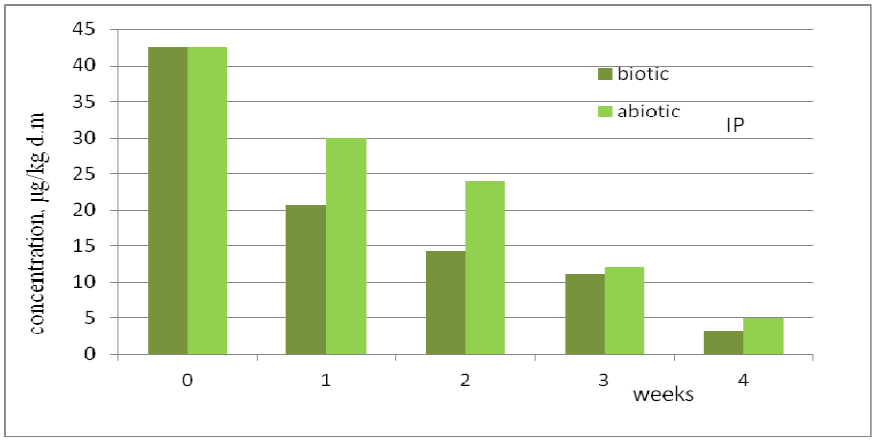

Fig. 5. Changes in the concentration of IP in sewage sludge (biotic and abiotic samples) during four weeks of incubation of incubation in light conditions

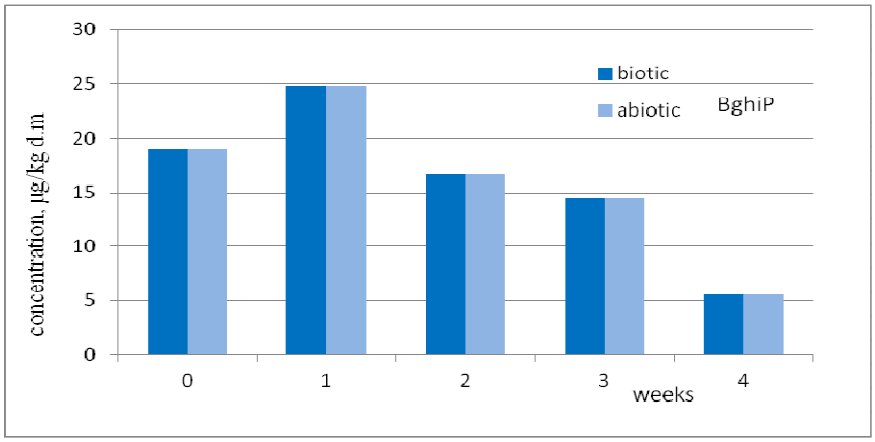

Fig. 6. Changes in the concentration of PghiP in sewage sludge (biotic and abiotic samples) during four weeks of incubation of incubation in light conditions

In the sludge samples stored under light conditions a decrease in 6-rings of PAHs concentration was at the same level and ranged 85% and 83% in biotic and in abiotic samples, respectively. During the incubation of sewage sludge fluctuation of PAHs concentration was observed. That may have been due to the release of PAHs from cells of microorganisms or the complex of organic associations [17-18]. The changes in the concentration of PAHs in sewage sludge amended with standard mixture incubated in light condition are given in Figures 7 and 8.

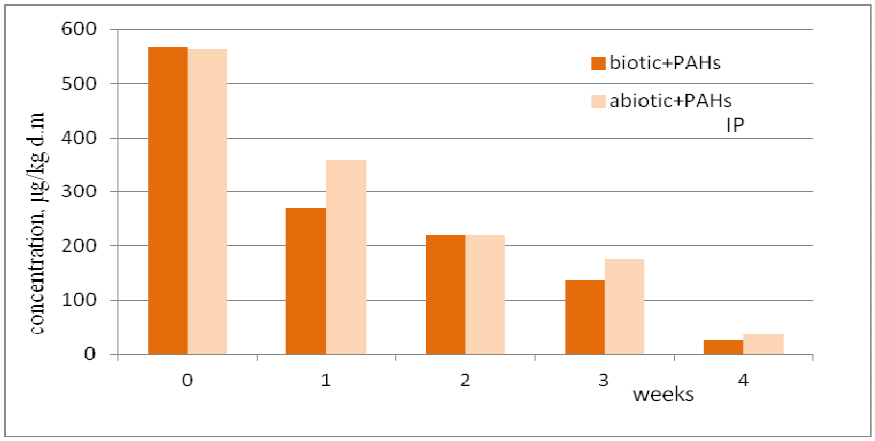

Fig. 7 Changes in the concentration of IP in sewage sludge (biotic and abiotic samples) amended with standard mixture during four weeks of incubation in light conditions

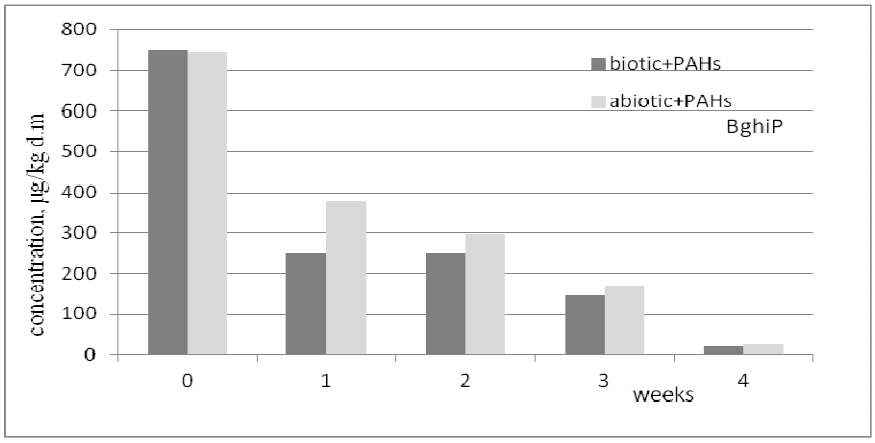

Fig. 8. Changes in the concentration of PghiP in sewage sludge (biotic and abiotic samples) amended with standard mixture during four weeks of incubation of incubation in light conditions

The gradually lower concentration of the two studied PAHs was determined during incubation of the samples under light conditions. In the final step of the investigation (after 4 weeks) the total PAHs concentration in the sewage sludge was lower than in the initial ones of 95-96% and did not depend on microorganisms presence. At the end of experiment the sum of 2PAHs concentration not exceed 74 µg/kg d.m. After four weeks of the experiment in the sewage sludge samples exposed UV rays the contents of IP and BghiP was lower than initial concentration. The final hydrocarbons concentration in the biotic and abiotic samples exposed to UV rays was lower than the initial

concentration of 90% and 85%, respectively. Changes in the concentration of indeno(1,2,3 c,d)pyrene and benzo(ghi)perylene during four weeks of incubation exposed UV rays are given in Figures 9-10.

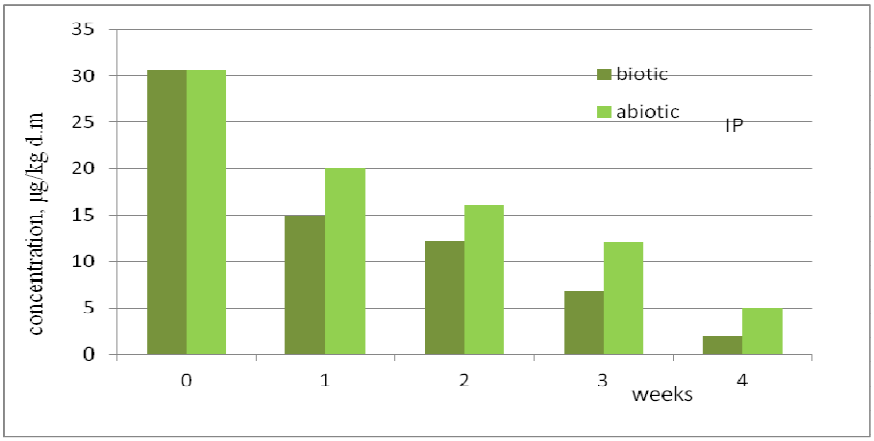

Fig. 9. Changes in the concentration of IP in sewage sludge (biotic and abiotic samples) during four weeks of incubation of incubation exposed UV rays

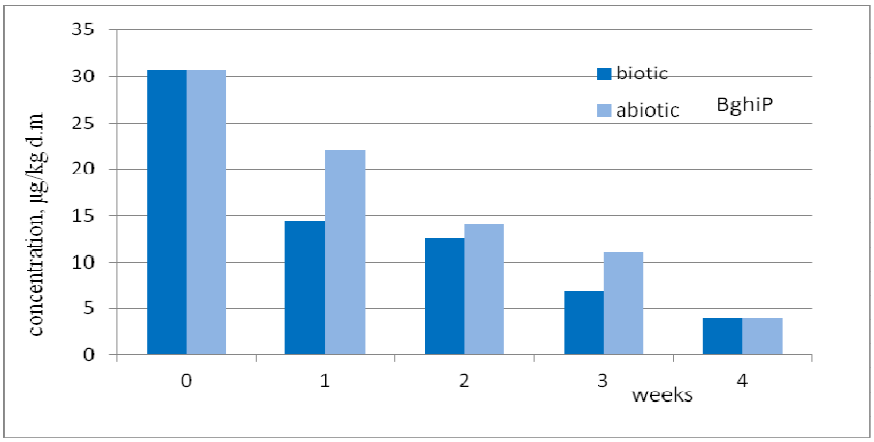

Fig. 10. Changes in the concentration of BghiP in sewage sludge (biotic and abiotic samples) during four weeks of incubation of incubation exposed UV rays

In Figures 11-12 the changes in the concentration of PAHs in sewage sludge amended with standard mixture incubated exposed under UV rays.

The dynamic of concentration changes of individual hydrocarbon in samples amended with standard mixture were similar. Changes in 6-ring hydrocarbons concentrations between the initial and final concentration were significantly in sewage sludges. In the final step of the investigation (after 4 weeks) the total

PAHs concentration in the sewage sludge was lower than in the initial ones of 96-97% and did not depend on microorganisms presence.

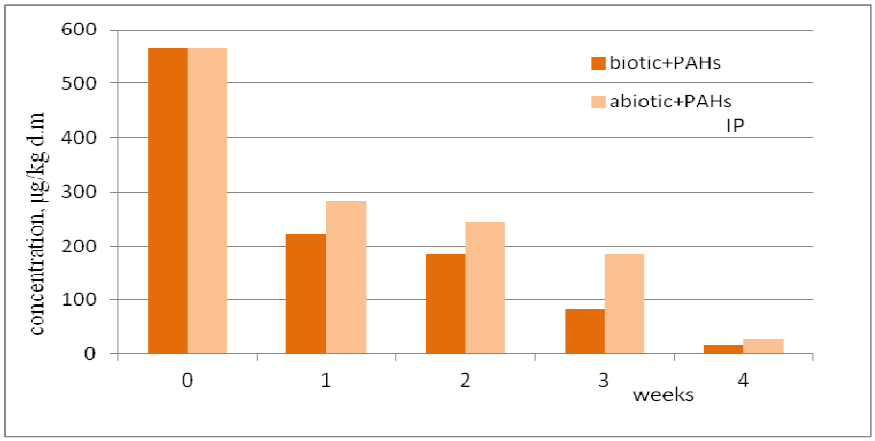

Fig. 11. Changes in the concentration of IP in sewage sludge (biotic and abiotic samples) amended with standard mixture during four weeks of incubation exposed UV rays

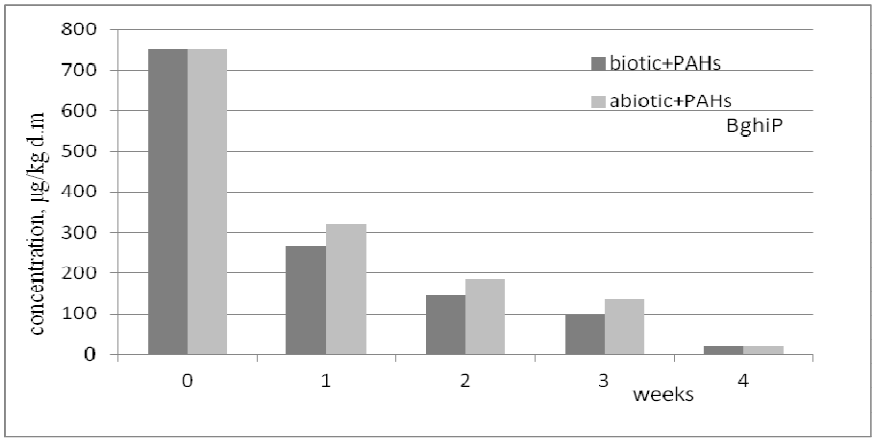

Fig. 12. Changes in the concentration of PghiP in sewage sludge (biotic and abiotic samples) amended with standard mixture during four weeks of incubation of incubation exposed UV rays

The studies proved that the process of PAHs degradation takes place much more difficult in sewage sludge without standard mixture. Therefore, it could be concluded that PAHs may be present not decomposed in the environment. That is very important in agricultural application of sewage sludge.

The statistical analysis shows that there are no significant differences in sludges augmented with the standard mixture among the concentration of hydrocarbons in the both sludges (without and with added sodium azide) while deposing sewage sludges. There is a significant difference between the total contents of two PAHs before and after incubation. The addition of sodium azide had a significant impact on the changes in 6-ring of PAHs concentrations whed the sewage sludge without light were stored. Therefore, statistical analysis shows the importance of abiotic processes in the loss of PAHs. This indicates the relatively low importance of biological effects in the removal of hydrocarbons. The addition of standard mixture had significant impact on changes of PAHs concentrations in the samples. Thus, it is suggested that investigations into the dynamic of changes of PAH concentration in sludges should be carried out without any additional amount of hydrocarbons. The results are similar to the scientific literary sources concerning the behaviour of PAHs' in soil and in the sewage sludge during the composting process. It is stated that the stability of individual hydrocarbons could vary and the dynamics of the concentration changes during incubation of the analyzed materials could be irregular. Irregular changes in the concentration of PAHs in digestion process (fermentation process, composting process) and in deposed sewage sludge were observed [19-20].

4. CONCLUSIONS

On the basis of the conducted investigation (under certain conditions) and obtained results it can be concluded that:

- significant differences between the initial concentrations and the final concentrations for indeno(123cd)pyrene and benzo(ghi)perylene in sewage sludge were observed.-
- the dynamics of hydrocarbons changes in sewage sludges supplemented with the standard mixture was similar to the one observed in the sludges both with and without sodium azide (in biotic and in abiotic samples).
- the most persistent of studied hydrocarbons occurred in the sewage sludge originating from the treatment plant stored without light access.

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BIOTYCZNY I ABIOTYCZNY ROZPAD INDENO-PIRENU I BENZO(GHI)PERYLENU W RÓŻNYCH WARUNKACH ŚWIETLNYCH

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

Celem badań było określenie zmian stężeń WWA w osadach ściekowych eksponowanych w różnych warunkach świetlnych. Osady ściekowe były przechowywane w warunkach tlenowych. Badania były prowadzone w warunkach laboratoryjnych, gdzie osady ściekowe były przechowywane bez dostępu światła, wystawione na działanie światła dziennego lub naświetlane promieniami UV. Zmiany stężenia WWA analizowano w czterech seriach: w osadach pobranych z oczyszczalni ścieków (próbki biotyczne), w osadach ściekowych z dodatkiem mieszaniny standardowej PAH (próbki biotyczne +WWA), w osadach z dodatkiem azydku sodu (próbki abiotyczne) oraz w osadach, do których wprowadzono mieszaninę standardową WWA oraz azydek sodu (próbki abiotyczne+WWA). Zmiany w stężeniu 6-pierścieniowych WWA (indeno 1 2 3cd)pirenu i benzo(ghi)perylenu) w osadach były kontrolowane w odstępach 7- dniowych przez 4 tygodnie. Stężenia WWA oznaczano z wykorzystaniem układu: chromatograf gazowy- spektrometr masowy GC-MS. Straty węglowodorów po 4 tygodniach badań były w granicach od 62 do 97%. Zależały od rodzaju próbki i analizowanego związku. W osadach ściekowych bez dodatku mieszaniny standardowej przechowywanych bez dostępu światła efektywność rozpadu WWA była w zakresie 60-75%.W osadach szczepionych dodatkową ilością WWA w postaci standardu, straty tych związków sięgały 97%. Końcowe stężenia WWA w próbkach biotycznych były mniejsze o 2-13% od stężeń tych związków w próbkach abiotycznych.

Słowa kluczowe: osady ściekowe, WWA, GC-MS, światło dzienne, promienie UV

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