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## IMPACT LOW-COST PROCESSING METHODS ON THE CONTENTS OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEWAGE SLUDGE

### WPLYW NISKONAKŁADOWYCH METOD PRZETWARZANIA NA ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W OSADACH ŚCIEKOWYCH

**Abstract:** In Poland, more and more often to the processing of sewage sludge are used low-input methods: composting, vermicomposting, reed bed, willow energy and solar driers. Also in the north-eastern part of Poland for many years successfully operate objects using these methods.

The paper presents the experience of the use of low-cost methods of sludge treatment in wastewater treatment plant located in Zambrow, Podlaskie Province. The results of studies of sewage sludge on the PAHs content after treatment in reed bed system were presented.

In 2012, samples of sediment were taken from the middle part of the oldest reed bed (still in service) in the 3-meter profile of the sediment fill. Sampling was performed using a special probe to enable the extraction of sewage sludge from the full depth of the lagoon. Samples were averaged and sediment samples from each 0.5 m section were tested.

The obtained results for the PAHs in sediments from the lagoon of sludge from reed sewage treatment plant in Zambrow show that the average content of PAHs studied is approximately  $5552.8 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$  At the same time, there are clear differences in the content of these compounds in each of the processed layers of sludge in the lagoon. An average contents of PAHs tested in individual layers of the sludge were as follows:  $5852.2 \mu\text{g PAHs} \cdot \text{kg}^{-1} \text{ d.m.}$  in the upper sludge layer (0–1 m),  $6636.8 \mu\text{g PAHs} \cdot \text{kg}^{-1} \text{ d.m.}$  in the middle sludge layer (1–2 m) and  $4169.5 \mu\text{g PAHs} \cdot \text{kg}^{-1} \text{ d.m.}$  in the oldest, bottom sludge layer (2–3 m). A significant decrease in the total PAHs content with increasing the time period of the processing of sludge lagoons at the lowest bottom layer was observed after 10–12 years. Sewage sludge processed by California earthworms for vermicompost was characterized by the lowest total content of studied PAHs, which amounted  $2550.2 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$

**Keywords:** polycyclic aromatic hydrocarbons, reed bed systems, sewage sludge

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## Introduction

In Poland, more and more often for processing of sewage sludge low-input methods are used, *ie*: composting, vermicomposting, reed bed, willow energy and solar driers. Also in the north-eastern Poland for many years facilities are operated, in which these methods are successfully used. This sector of wastewater treatment is affected by the following factors:

- majority of waste treatment plants are small and medium-sized facilities,
- agricultural and industrial character of the region,
- character of generated sewage sludge,
- available on these areas biomass as straw, sawdust and chips,
- low quality class of the soil [1].

All these factors justify the possibility of using low-input processes on these areas.

Low-input methods of processing sewage sludge are characteristic first of all by their simple design and technology and by their easy operation. These methods allow using only a limited number of process equipment due to which the consumption of electrical energy is low. Utilisation of natural processes occurring in the environment allows maintaining low operation costs [2].

This paper presents selected examples of experience and the study of one of the first wastewater treatment plants in the Podlaskie Province in Zambrow run by the Zambrowskie Ciepłownictwo i Wodociągi sp. z o.o. (District Heating and Waterworks Zambrow Ltd), which for a dozen or so years successfully treats sewage sludge by low-cost methods [3]. The goal of the study was first of all to verify if using reed bed lagoons and vermicomposting for the PAHs decomposition process is efficient.

From the ecological point of view more important is the PAHs collection and transformation within individual ecosystems. Since nearly 90 % of the PAHs contained there come from the soil specific actions and means should be implemented to protect these ecosystems. Moreover studies so far demonstrate differences in the degree and the speed of the PAHs transformation in the soil, what proves their long life and the possibility of bioaccumulation in this environment. The PAHs (and other organic compounds) occur also in plants, thus being a great concern, as the mechanism of absorbing the PAHs and other organic compounds is not fully understood. It is assumed that it is possible due to accumulation of harmful substances on the surface of leaves during atmospheric precipitations or due to contamination with soil particles. Irrespective of that in many countries studies are conducted in order to determine the limit values for organic substance content both in sewage sludge and in composts and in potable water. In Germany there are no binding regulations concerning the PAHs content in sludge, however, a designation of 9 PAHs is recommended; the sum of which should not exceed  $6000 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$  In the proposed amendment to the Sediment Directive the sum of 11 hydrocarbons should not exceed  $6000 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$

The Polish legislation does not provide any regulations on the maximum PAHs content in sewage sludge designed for use in the agriculture as well as there is no uniform procedure of analytic analysis of PAHs in sludge. Determination of micro-contaminations in the sewage sludge is one of the most complicated analytical tasks connected with the heterogeneity of these materials and with differentiated PAH concentrations [4].

PAHs are also in the air as vapor and aerosols defaulting on dust particles [5].

Although the PAHs content in sediments used in agriculture in Poland is not subject to norms these substances are taken into account in the draft of alterations / amendments to the UE Directive 75/442/EEG according to which a permissible summary concentration of 11 aromatic compounds (acenaphthene, phenanthrene, fluorene, fluorantene, pyrene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene) should be  $6 \text{ mg} \cdot \text{kg}^{-1}$  (converted to dry mass) [6].

## Material and methods

### Sludge management in a wastewater treatment plant

In the municipal wastewater treatment plant of the Zambrow city some 1 ton d.m. of raw sewage sludge is generated per full day. The sludge management is based on sludge lagoons, reed beds and earthworm fields. Outside of the winter season 70 % of the sludge is carried away directly to a reed bed of an area 3 times  $3500 \text{ m}^2$ . In winter the sludge is directed onto sludge lagoons provided with a vertical drainage ensuring a high efficiency of the sludge dewatering when filling the lagoon. In the wastewater treatment plant there are 2 sludge lagoons of a  $2500 \text{ m}^3$  capacity each. Approximately 80–90 % of the sludge collected on sludge lagoons is pumped in summer time onto earthworm fields of an area of some 1 ha. The remaining sludge is utilised in the agriculture, for reclamation in autumn (after harvest). This solution allows shortening the time of the sludge removal from the wastewater treatment plant down to two weeks, *ie* during emptying the sludge lagoon and after removing the sludge from earthworm fields during a period when this product is needed. Figure 1 illustrates the schematic of sludge in wastewater treatment plants in Zambrow.

In 2013 the sludge from the oldest reed lagoon will be removed after 14 years of operation.

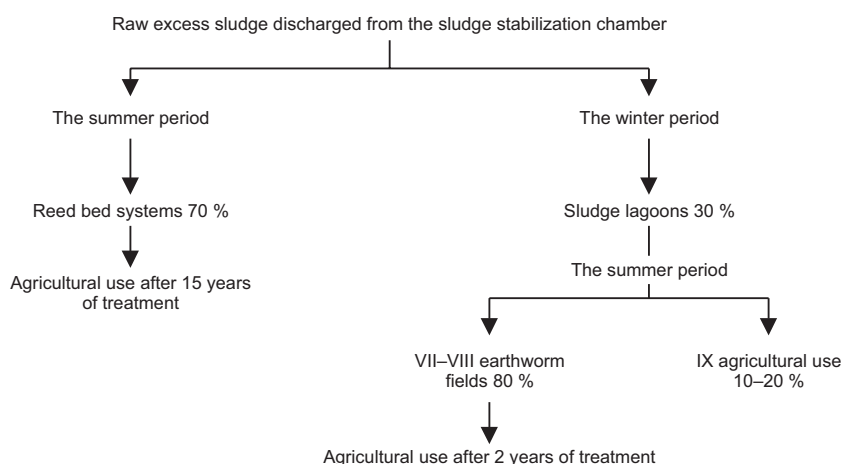


Fig. 1. Schematic of sludge in wastewater treatment plants in Zambrow

In 2013 sludge samples were taken from the middle oldest part of the operated lagoon in its 3 meter deep profile filled with the sediment. For every 0.5 m long section sludge samples were averaged and subjected to physio-chemical examination.

The method of designation of the content of selected PAHs in the biomaterial (sewage sludge) includes the way of determination of selected PAHs (Table 1) in a biomaterial of a concentration higher than  $1.0 \text{ ng} \cdot \text{g}^{-1}$  of dry mass (of every single compound) by a high performance liquid chromatography (HPLC) with the fluorescence detection after the ultrasound extraction.

Table 1

Polycyclic aromatic hydrocarbons identified by this procedure

No.	Name of substance	Chemical formula	Molecular weight [ $\text{g} \cdot \text{mol}^{-1}$ ]	Carbon participation [%]
1	fluoranthene	$\text{C}_{16}\text{H}_{10}$	202.26	95.0
2	benzo(b)fluoranthene	$\text{C}_{20}\text{H}_{12}$	252.32	95.2
3	benzo(k)fluoranthene	$\text{C}_{20}\text{H}_{12}$	252.32	95.2
4	benzo(a)pyrene	$\text{C}_{20}\text{H}_{12}$	252.32	95.2
5	dibenzo(a, h)anthracene	$\text{C}_{22}\text{H}_{14}$	278.35	94.7
6	benzo(g, h, i)perylene	$\text{C}_{22}\text{H}_{12}$	276.34	95.6
7	indeno(1,2,3-cd)pyrene	$\text{C}_{22}\text{H}_{12}$	276.34	95.6

The method consisted in separation of PAHs from a biological matrix by an ultrasound method using an appropriate organic solvent (benzene) and in designation of tested compounds by the high performance liquid chromatography (HPLC). The extract was concentrated by evaporation in a nitrogen jet and the remnant was dissolved in an organic solvent (acetonitrile). Next, the PAHs mixture was separated in a chromatography column by way of the gradient elution. The identification and quantitative designation was performed by the fluorescence detection with programming of the wave of excitation and emission.

The identification of individual PAHs was carried out comparing the retention times of the sample peaks to the peak retention times from reference solutions by the method of a reference curve with addition of an examined matrix.

It is a different methodology than that used for the determination of PAHs in marine waters [7].

## Results and discussion

The Table 2 presents averaged results of the PAHs study. The content of the following PAHs were determined in the sewage sludge: naphthalene, anthracene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. Designations used in the Table 2: I – depth 0.0–0.5 m, II – depth 0.5–1.0 m, III – depth 1.0–1.5 m, IV – depth 1.5–2.0 m, V – depth 2.0–2.5 m, VI – depth 2.5–3.0 m, W – vermicompost.

Table 2

The results of dewatered sludge in the lagoon cane and vermicompost processed by California earthworms for the content of PAHs

PAH [ $\mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$ ]	No.	I	II	III	IV	V	VI	W
Naphthalene		277.1	276.6	266.3	266.1	265.5	265.5	35.1
Anthracene		203	199	132	98.6	79.6	83.4	32.4
Fluoranthene		1630	1542	1496	1454	912	821	163.6
Benzo(b)fluoranthene		823	708	812	889	312	407	543.2
Benzo(k)fluoranthene		566	502	538	579	434	334	432.1
Benzo(a)pyrene		723	718	823	848	654	474	732.2
Dibenzo(a, h)anthracene		42.3	37.3	53	60.7	29	26	34.2
Benzo(g, h, i)perylene		865	892	1213	1319	934	864	176.1
Indeno(1,2,3-cd)pyrene		876	824	1127	1299	827	617	401.3
Total PAHs		6005.4	5698.9	6460.3	6813.4	4447.1	3891.9	2550.2

Source: Research and development of their own.

The (Fig. 2 and 3) illustrate the changes in the concentration of individual PAHs and their total deposits in the studied samples as a function of the processing time in the lagoon cane.

9 PAHs were found out in all examined samples. Referring the test results to the above-mentioned Directive excessive values were found out in three samples of the

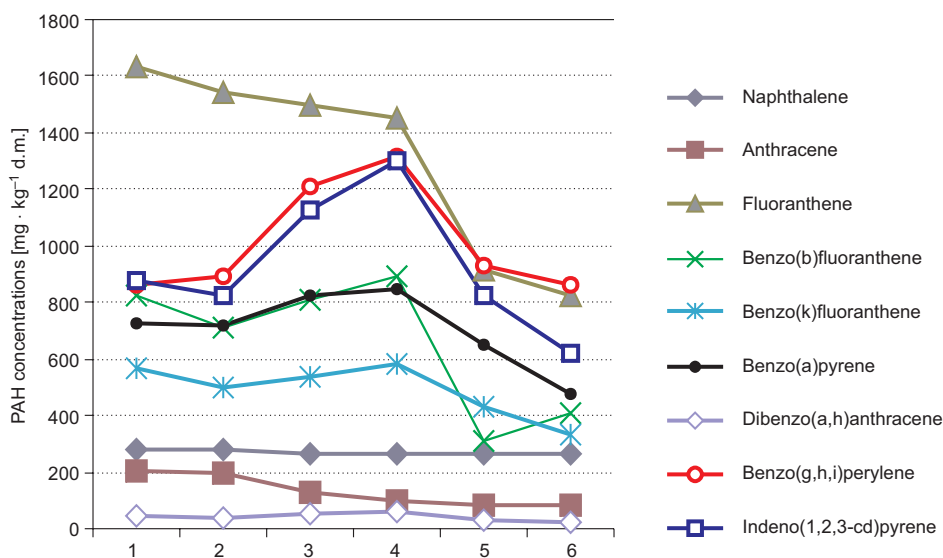


Fig. 2. Changes in concentration of individual PAHs studied depending on the processing time of sludge in the lagoon cane. Source: own research

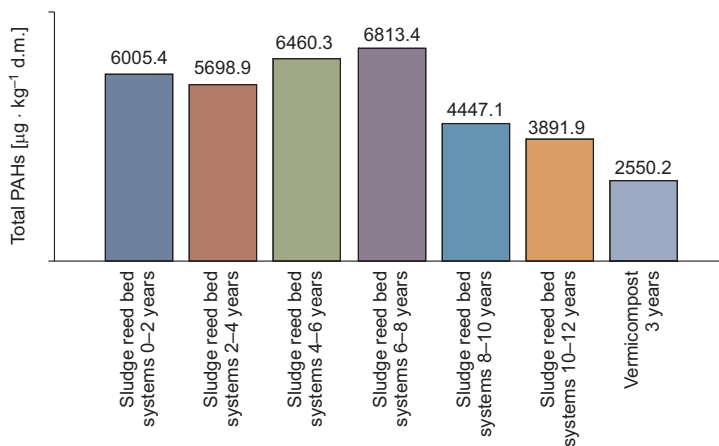


Fig. 3. Total studied PAHs content in sewage sludge, depending on the time of its lagoon cane processing. Source: own research

sediment from the reef lagoon. For sediments from a 2, 6 and 8-year time of transformation the total of the examined PAHs exceeded  $6 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$  In samples of the lowest sediment lagoon layers from the 10–12-year period of operation the lower concentration of the tested PAHs were found out; correspondingly at  $4.4471 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$  for sediments transformed for 10 years and at  $3.8919 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$  for sediments transformed for 12 years. The lowest sum of tested PAHs was obtained for the 3–7-year vermiculture –  $2.5502 \text{ mg} \cdot \text{kg}^{-1}$  converted to dry mass.

Among the 9 examined PAHs of the lowest concentration was the dibenzo(a,h)anthracene, the concentration of which in not a single sample exceeded  $100 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$  The highest concentration was determined in case of fluoranthene and benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene; the concentration of these compounds exceeded  $1000 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$  (Fig. 1).

Włodarczyk-Makula [8] has studied for the PAHs content in the soil from the Czestochowa region as well as in the sewage sludge. The sum of 16 PAHs is much lower than in sewage sludge from Zambrow as it does not exceed  $1.912 \mu\text{g} \cdot \text{g}^{-1} \text{ d.m.}$ , from which 60 % in three examined samples were found naphtalene and acenaphtylene. On the other hand the Zambrow sewage sludge are characterised by their low content of naphtalene, below 7 % of the PAHs sum. Bodzek [9] obtained similar results examining sewage sludge in Gorny Slask (Upper Silesia) since the sum of tested two-ring hydrocarbons, *ie* the naphtalene and dimethyl-o-phenyl did not exceed  $0.3 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$

The benzo(b)fluoranthene was found in the majority of sludge samples and its highest concentration was determined in the reed lagoon after 8 years of transformation at the level of  $889 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$  and in the 3-year old vermicompost at the level of  $543.2 \mu\text{g} \cdot \text{kg}^{-1} \text{ d.m.}$ , which was 13 % to 21 % of the 9 PAHs sum. Perez [10] obtained approximate levels examining sewage sludge in Spain for the PAHs content. Measurements were carried out with the gas chromatograph and showed a relatively high

concentration of benzo(b)fluoranthene –  $746 \mu\text{g} \cdot \text{kg}^{-1}$  d.m., thus constituting 26 % of the 16 PAHs sum.

The concentration of the naphthalene in case of sludge from the reed field ranged from 265.5 to  $277.1 \mu\text{g} \cdot \text{kg}^{-1}$  d.m. Results obtained by Oleszczuk [11], who examined the PAHs concentration in sludge from the reed field at a dose of 600 ton of the sewage sludge per 1 hectare, are somewhat different. He obtained the naphthalene concentration within  $0.0054$  to  $0.0089 \mu\text{g} \cdot \text{kg}^{-1}$  d.m.

The benzo(g,h,i)perylene concentration in samples from the reed bed lagoon ranged from 864.1 to  $1319.1 \mu\text{g} \cdot \text{kg}^{-1}$  d.m. but in case of a 3-year vermicompost was found the lowest value –  $176.1 \mu\text{g} \cdot \text{kg}^{-1}$  d.m. The PAHs concentration drop with time of composting is confirmed also by the study of Oleszczuk [12] on the example of the same hydrocarbon studied in Krasnik, where the initial value was  $719.9 \mu\text{g} \cdot \text{kg}^{-1}$  d.m., and already after 76 days only  $267.8 \mu\text{g} \cdot \text{kg}^{-1}$  d.m.

The results of the study demonstrate a high efficiency of low-cost methods used in the wastewater treatment plant in Zambrow in terms of the quality of processed sludge. Sewage sludge from the lowest layer of the reed lagoon (12–13-year of dewatering and transformation) are characterized by the lowest PAHs content. The higher a sediment layer lies, *ie* the shorter the time of processing, the higher is the PAHs content. This points to a great role of reed in accumulation of these compounds. Concerning the PAHs content in the produced compost its highest reduction was observed. A three-year processing of sludge by Californian earthworms allows achieving lower PAHs content as compared to a dozen or so years of sludge dewatering on a reed bed lagoon. This is also confirmed by other national and foreign experiments [13–15].

## Conclusions

The wastewater treatment plant in Zambrow is the only facility in the Podlaskie Province in which exclusively natural, low-input methods of the sediment processing are used. On the example of solutions used in Zambrow one can state that for selection of methods of sewage sludge processing, especially such which promise to meet the conditions for the use in the nature or agriculture, also such factors as the process cost, the final utilization of the sewage sludge, the analysis risk and the environmental impact must be taken into account.

Conducted studies to determine the character of the sewage sludge from the wastewater treatment plant in Zambrow as well as effects achieved using the vermiculture and reed lagoons confirm that from the economic, ecological and environmental points of view these methods are justified. An important issue is the psychological factor, which will help to understand that the sewage sediment when properly transformed is not a dangerous waste but can be a competitive product.

According to the draft of alterations / amendments to the UE Directive 75/442/EWG excessive inadmissible concentration levels of the sum of 9 examined PAHs were stated in three samples of sewage sediments processed on a reed lagoon.

The lowest summary concentration of 9 PAHs was stated in a sewage sediment from the installation with a 3-year vermiculture, which means that vermicomposting can contribute to the reduction of the PAH concentration.

The study results indicate that the greater the number of rings in a given hydrocarbon the more difficult is the process of its mineralisation.

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**Abstrakt:** W artykule przedstawiono wyniki doświadczeń z zastosowaniem niskonakładowych metod przetwarzania osadów w oczyszczalni ścieków położonej w Zambrowie, województwo podlaskie. Zostały



przedstawione wyniki badań osadów ściekowych na zawartość WWA po przetworzeniu w lagunach trzcinowych oraz wermikulturę.

Uzyskane wyniki zawartości WWA w osadach z laguny trzcinowej z oczyszczalni ścieków w Zambrowie pokazują, że średnia zawartość WWA wynosiła  $5552,8 \mu\text{g} \cdot \text{kg}^{-1}$  s.m. Jednocześnie istnieją wyraźne różnice w zawartości tych związków w każdej z przebadanych warstw osadu w lagunie. Górna warstwa osadu (0–1 m) zawiera średnio  $5852,2 \mu\text{g} \cdot \text{kg}^{-1}$  s.m. badanych WWA, środkowa warstwa osadu (1–2 m) zawiera średnio  $6636,8 \mu\text{g} \cdot \text{kg}^{-1}$  s.m., a najstarsza dolna warstwa osadów (2–3 m) wskazuje średnio najmniejszą zawartość  $4169,5 \mu\text{g} \cdot \text{kg}^{-1}$  s.m. WWA. Zaobserwowano wyraźne zmniejszenie zawartości sumy WWA wraz z wydłużaniem okresu czasu przetwarzania na lagunach w najniższej dolnej warstwie osadu stwierdzoną po 10–12 latach. Osad ściekowy przetworzony przez dżdżownice kalifornijskie na wermikompost charakteryzował się najmniejszą zawartością sumy badanych WWA, wynoszącą  $2550,2 \mu\text{g} \cdot \text{kg}^{-1}$  s.m.

**Słowa kluczowe:** WWA, laguna trzcinowa, osady ściekowe

