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Municipal Sewage Sludge Processing Method Effect on the Content of Polycyclic Aromatic Hydrocarbons

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1. Introduction

According to the GUS "Environmental Protection 2016" study, in 2015, 951.5 thousand tons of sewage sludge dry matter was produced in Poland. At the end of the same year, the amount of sludge accumulated in the sewage treatment plant was 6,483.9 thousand tons. Nowadays, many wastewater treatment plants are struggling with a steadily increasing amount of sludge. Each of these objects selects the processing method and final disposal of sewage sludge on the basis of its own capabilities. Stabilized sewage sludge may be used for natural or energetic purposes. These capabilities are sometimes limited by the presence of pollutants which, when released, may have a negative impact on the environment and ultimately on humans. These include polycyclic aromatic hydrocarbons (PAHs) and heavy metals (Boruszko 2013, Boruszko et al. 2015). The natural use of the sewage sludge may cause that these pollutants accumulate in the soil, transfer to waters and plants intended for consumption or feed (Ociepa-Kubicka 2012). The Environment Minister Regulation from February 6th 2015 on municipal sewage sludge (Journal of Laws 2015, item 257) specifies the parameters that must be met by sewage sludge used naturally, including agricultural use. These are 10 indicators that do not include PAHs. These compounds show low degradability and are classified as persistent organic pollutants (POPs) according to Regulation (EC) No 850/2004 of the European Parliament and of the Council of 29 April 2004 (Banach-Szott et al. 2012). PAHs are compounds composed of benzene rings (from two to more than a dozen) and alkyl substituents. They have a strong affinity to particulate matter and are poorly soluble in water, so they easily adsorb on the surface of sewage sludge (Macherzyński et al. 2015). PAHs are deposited in sewage sludge as a result of accumulation and bioaccumulation from domestic and industrial wastewater. The concentration of individual hydrocarbons in industrial wastewater depends on the type of industry. The industry which supplies the largest quantities of these compounds in sewage includes power plants, coking plants, coal and crude oil processing (Janosz-Rajczyk et al. 2006). PAHs may be discharged into domestic sewage along with rainwater. They contain pollutants from, among other things, the atmosphere, asphalt and car tires. In sewage sludge, PAHs can also be formed spontaneously through the transformation of complex carbon compounds, e.g. during septic tanks (Janoska et al. 1993). Despite the persistence of these compounds, their decomposition in the environment is possible. The effectiveness of PAH decomposition depends on the number of benzene rings in their structure, the ability of existing microorganisms to degrade these compounds and environmental conditions, such as the presence of oxygen, temperature, UV radiation and water content (Włodarczyk-Makła 2014). The U.S. EPA recommends that 16 PAH compounds be determined in environmental samples: naphthalene, acenaphthene, acenaphthene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthr-axcene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene. The benzo(a)pyrene belonging to this group is considered to be the most important indicator of PAH presence in the environment (Kubiak 2013). According to the International Agency for Research on Cancer (IARC), it is the main human endangering carcinogen.

The aim of the study was to determine the content of PAHs and the share of particular groups of PAHs in municipal sewage sludge at particular stages of their production and processing in municipal sewage treatment plants.

2. Object and methods

The research was carried out on the basis of sludge samples taken from the wastewater treatment plant in Białystok. The mechanical-biological treatment plant in Bialystok was launched in 1994. The last modernization was completed in 2008. The operation of the plant is based on the technology of active sludge divided into three nodes: mechanical, biological and sludge processing. About 80% of the amount of inflowing sewage is domestic wastewater, 20% is industrial wastewater. Their source is the town of Białystok and the communes adjacent to the town. The treated wastewater is discharged to the Biała River. According to the KPOŚK (National Urban Wastewater Treatment Plan) report of 2015, the actual PE of the facility is approximately 360,000, of which 56,200 is for industry. The maximum capacity of the plant is 450,000 PE. The planned flow capacity of the plant is 100,000 m^3/d. The reduction of incoming pollutants is estimated at 95% BOD, 90% total nitrogen, 96.8% total phosphorus and 85% total suspended solids. Sewage sludge is thickened and then fermented in four separate fermenters. The process takes place for 25-30 days at 35-37°C. Ultimately, the sludge is dewatered, and part of it is thermally dried and converted into pellets. It is used for fertilization and soil reclamation. Every year, 6800 tons of dry sludge mass is produced at the plant.

Sludge samples were collected in three research cycles: autumn (November), winter (February) and spring (April) in 2017 and 2018. In each cycle the samples of preliminary sludge, excess sludge from the press, digestate and dewatered digestate sludge were analyzed. For each sludge, 3 samples were taken for further testing. The samples were analyzed for concentration of 16 PAHs (naphthalene, acenaphthene, acenaphthene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene), benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)-anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene) at the Faculty Chemical Laboratory of the Bialystok University of Technology. For this purpose, gas chromatography combined with mass spectrometry using the GC/MS Agilent 7890B chromatograph was used. The results were given as single compounds of PAHs, which were then grouped according to the number of aromatic rings. The results of PAH content in individual groups were subjected to statistical calculations. The changes occurring in the set of variables were analyzed using the Fisher's least significant differences test. The qualitative factor in the analysis of variance was the series of studies (after extraction) and the type of sludge. All the variables used in the analysis were characterized by normal distribution according to the Saphiro-Wilk test and homogeneity of variance according to Bartlett's test.

3. Results and discussion

The sum of PAHs in the analyzed sludge samples depended more on the timing of sampling of individual samples than on the type of sludge (Tab. 1). The average summary content of these compounds was the highest in the preliminary sludge in comparison to other sludge samples. Research on unprocessed sewage sludge was conducted by researchers in Poland and in other countries.

Oleszczuk (2009) showed a content of 16 EPA PAHs in sludge in the range from 2.83 mg/kg d.m. to 9.95 mg/kg d.m. and Li and others (2008) showed a content at a very high level from 88.81 mg/kg d.m. to 100.74 mg/kg d.m., a lower content was found in studies of sludge samples from China which ranged from about 0.5 mg/kg d.m. to 3.6 mg/kg d.m. (Feng 2008, Liu 2013). In research conducted in Scandinavia, Paulsrud et al. (1997) found a very broad range of 16 PAHs in sewage sludge from 1.0 mg/kg d.m. to 30 mg/kg d.m. Different contents result from sewage quality flowing into the treatment plant. In excessive sludge and after the fermentation process, the content of total PAHs was similar and lower than in preliminary sludge. The least of these compounds occurred in the sludge after fermentation and dehydration. The preliminary and dehydrated sludge was dominated by four-ring hydrocarbons, while the excess and after fermentation were dominated by three- and four-ring hydrocarbons.

Table 1. The content of PAHs with a given number of rings in the analyzed sewage sludge in mg/kg d.m.

Sample No	Sludge type	Series	Number of rings					Sum
			2	3	4	5	6	
1	Preliminary sludge	I	0.10	0.72	0.84	0.49	0.00	2.16
		II	0.10	1.09	2.26	1.00	0.67	5.12
		III	0.21	0.61	1.28	0.77	0.52	3.39
		mean	0.14	0.81	1.46	0.76	0.40	3.77
2	Excess sludge after press	I	0.03	2.58	2.35	0.39	0.00	5.35
		II	0.05	0.35	0.43	0.29	0.08	1.20
		III	0.05	0.87	0.60	0.26	0.08	1.86
		mean	0.04	1.27	1.12	0.31	0.05	2.83
3	Sludge after fermentation	I	0.13	1.75	1.89	0.37	0.00	4.14
		II	0.10	0.44	0.59	0.35	0.22	1.69
		III	0.11	1.06	0.80	0.40	0.23	2.59
		mean	0.11	1.08	1.09	0.37	0.15	2.88
4	Sludge after fermentation and dehydration	I	0.04	0.55	1.62	0.67	0.70	3.59
		II	0.07	0.29	0.38	0.22	0.21	1.17
		III	0.04	0.33	0.25	0.23	0.11	0.96
		mean	0.05	0.39	0.75	0.37	0.34	1.94

Most of the six-ring hydrocarbons were in the sludge after dehydration. Only for some of the compounds, statistically proven relationships were found and they occurred between the content of the tested PAHs in the case of 2-ring compounds between the preliminary sludge and the excessive sludge and dehydrated fermented sludge, and between the excessive sludge and the preliminary sludge and dehydrated fermented sludge. Further statistically proven differences were observed in the case of 5-ring compounds and they occurred between the preliminary sludge and the other investigated types of sludge. No statistically significant differences were observed in the case of 3, 4 and 6-ring compounds. Changes in the content of PAHs in sewage sludge during their processing with biological methods are indicated by many authors (Stringfellow 1999, Lu et al. 2013, Palani-samii in 2012, Villar et al. 2006). Some authors point to the presence of organic solvents that cause an increase in PAHs content in sludge. PAHs may also form in sludge spontaneously, in example during rotting processes, as a result of varying composition organic matter biotransformation. Fermentation of the investigated sludge did not contribute to the increase of PAH content in comparison to excessive sludge.

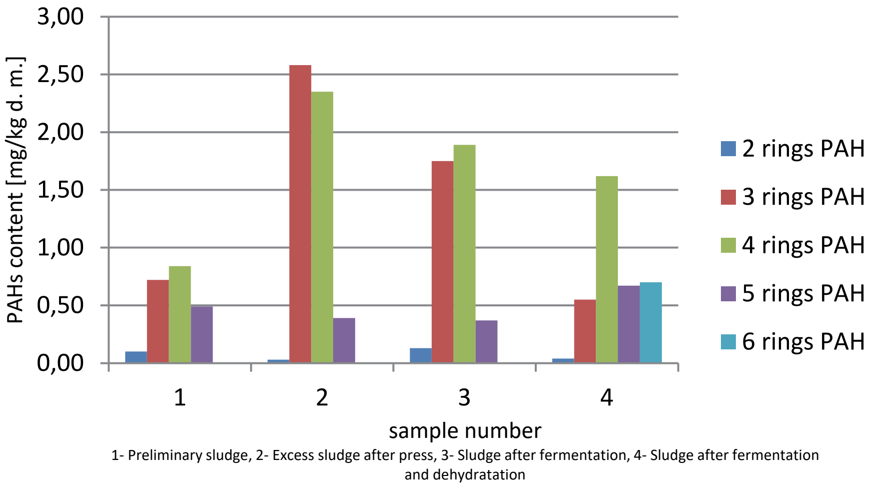

Fig. 1. PAH content in sewage sludge – autumn series

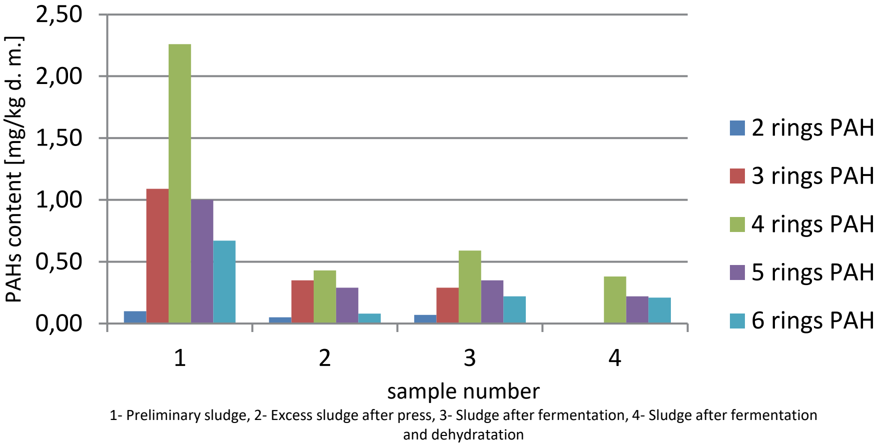

Fig. 2. PAH content in sewage sludge – winter series

The content of individual PAH groups in the investigated sludge was at a very different level depending on the series of studies, although no statistical differences between the terms (series) of sludge collection for individual PAH groups in the sludge were proved (Fig. 1, 2 and 3). Their highest amounts were recorded in series I (autumn). The content of 16 PAHs in this period was 5.4 mg/kg d. m. for excessive sludge, 4,1 mg/kg d. m. for digestate and 3,6 mg/kg d. m. for dehydrated sludge after fermentation. The exception was the preliminary sludge, in which the highest value of PAH was observed in winter (5.1 mg/kg d. m.). The highest share in the total content of PAH in the examined samples was found in three- and four-ring compounds (20.2- 44.9% and 38.7-39.8%, respectively). In the conducted studies, this correlation was observed for the winter and spring series (increase from 1.2 mg/kg d. m. in excessive sludge to 1.7 mg/kg d. m. in fermented sludge for the winter series and from 1.9 mg/kg d. m. to 2.6 mg/kg d. m. for the spring series). In the autumn series, the digested sludge contained slightly less PAH than the excessive sludge. For all series, the overall PAH content of the dehydrated digestate turned out to be lower than that of the excessive sludge.

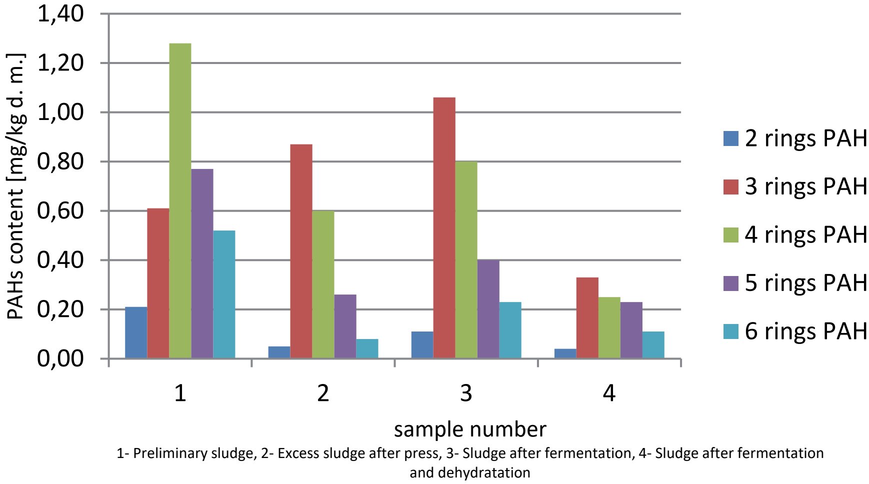

Fig. 3. PAH content in sewage sludge – spring series

In the autumn series the amount of PAH decreased by 33%, in the winter series only by 2.24% and in the spring series by 48.19%. This means that the content of PAHs in the analysed sludge decreased after processing. Similar results were obtained by Boruszko et al. (2015) and Włodarczyk-Makła (2010). According to the research carried out by the Institute of Environmental Protection for the treatment plant of Podlaskie Voivodeship in 1998-2000, the content of polycyclic aromatic hydrocarbons in sewage sludge in that period ranged from 2.6 to 17 mg/kg d.m. Comparing the results obtained (0.96-5.4 mg/kg d. m.) with those of previous years, it can be stated that the sum of PAHs in sewage sludge decreased.

Fluoranthene (8.65-17.92%), pyrene (7.54-16.30%) and phenanthrene (3.87-22.92%) were the dominating compounds. The advantage of fluoranthene, anthracene and pyrene over other PAHs in sewage sludge was found by Włodarczyk-Makuła et al. (2010). The content of benzo(a)pyrene, considered to be the most toxic aromatic hydrocarbon, was found in preliminary sludge. In the autumn series its content was 118 mg/kg d. m., and in the spring series 302 mg/kg d. m.. In the first series of studies, practically no six-ring PAHs were observed – only in the digested sludge after dehydration their value was 0.70 mg/kg d. m. It is assumed that a characteristic feature of PAHs is their increased release in the methane fermentation process (Włodarczyk-Makuła et al. 2010, Boruszko et al. 2015, Macherzyński et al. 2015). Studies on Oleszczuk and Baran (2004) show similar trends in the behaviour of PAHs in sludge. Authors found that the most mobile and at the same time the most susceptible to microorganisms, fungi and enzymes are hydrocarbons with the smallest number of aromatic rings in the particle. They show weaker hydrophobic properties than 5- and 6-ring PAHs and are less likely to bind to solid particles and therefore more bioavailable. On the other hand, PAHs with more rings and thus higher molecular weight are absorbed by the solids of the sludge and are characterised by low mobility (Marusenko et al. 2011). The authors claim that the fermentation process lowers the content of PAHs in the sludge, but the conducted studies do not confirm this relationship, the content of analyzed hydrocarbons in the digested sludge was similar to the content in the excess sludge.

In Poland, there are currently no provisions in place to limit the amount of PAHs in sewage sludge. The European Commission is planning to amend Directive 1986/278/EEC, which would set the required values for these pollutants to be met by sludge used in agricultural. It is proposed to establish the sum of 11 PAHs: acenaphthene, phenanthrene, fluorene, fluoranthene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, ben-zo(g,h,i)perylene and indeno(1,2,3-cd)pyrene. This value could not exceed 6 mg/kg d.m. of sludge. In case of the analyzed sludge, the highest total value of 16 PAHs was found in the excessive sludge during the autumn season (5.4 mg/kg d.m.). In terms of PAH content, the analyzed sludge can therefore be considered safe.

4. Conclusion

1. The 16 PAHs sum content depended on the type of sewage sludge and the highest was found in the preliminary sludge.
2. The process of fermentation, or rather dewatering of sludge after fermentation, lowered the content of 16 PAHs. Processing method affected the share of hydrocarbons in particular groups.

3. The share of individual PAH groups in terms of rings number depended on the season in which the sludge was collected for analysis.
4. The sludge samples were dominated by a group of three- and four-cyclic hydrocarbons, with the least amount of two- and six-cyclic hydrocarbons.
5. All investigated sludge samples did not exceed the normative content for the sum of 11 PAHs proposed by the European Commission for sludge used for agricultural purposes.

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Abstract

The aim of the study was to determine PAH content and the share of their individual groups in municipal sewage sludge at individual stages of their production and processing in a municipal wastewater treatment plant. Sludge samples were collected in three study cycles: autumn (November), winter (February) and spring (April) in 2017 and 2018. In each cycle the samples of initial sludge, excessive sludge after press, digestate sludge and digested dehydrated sludge were analyzed. Three samples were taken from each sludge for further analysis. The content of 16 PAH (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)-pyrene, dibenzo-(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-c, d)pyrene) was determined in the samples in the Faculty Chemical Laboratory at Białystok University of Technology. For this purpose, a gas chromatography method coupled to mass spectrometry using a GC/MS Agilent 7890B chromatograph was used. The results were given as single PAH compounds, which were then grouped by the number of aromatic rings. It was found that the total content of 16 PAHs depended on the type of sewage sludge and the highest one occurred in the initial sludge, and much lower in other sediments. The fermentation process, and more drainage of the fermentation sludge, reduced the content of 16 PAHs. The transformation processes had an influence on the hydrocarbon content in particular groups. The share of PAH groups depending on the number of rings in total 16 depended on the date of collection of studied sludges. In the studied sludges, a group of three and four-ring hydrocarbons dominated, and the least was two- and six-ring hydrocarbons. PAH content in all analyzed sludges did not exceed the norm for the total of 11 PAHs proposed by the European Commission for sludge used for agriculture.

Keywords:
PAH, sewage sludge, sludge disposal

Wpływ przeróbki osadów ścieków komunalnych na zawartość wielopierścieniowych węglowodorów aromatycznych

Streszczenie

Celem pracy było określenie zawartości WWA i udziału poszczególnych grup w komunalnych osadach ściekowych na poszczególnych etapach ich produkcji i przetwarzania w oczyszczalni ścieków komunalnych. Próbki osadów pobrano w trzech cyklach badań: jesienią (listopad), zimą (luty) i wiosną (kwiecień) w 2017 i 2018 roku. W każdym z cykli badano próbki osadu wstępnego, osadu nadmiernego po prasie, osadu przefermentowanego i osadu przefermentowanego poddanego dehydratacji. Z każdego osadu pobrano trzy próbki do dalszej analizy. Zawartość 16 WWA (naftalen, acenaften, acenaften, acenaften, fluoren, fenantren, antracen, fluoranten, piren, benzo(a)antracen, chryzen, benzo(b)fluoranten, benzo(k)fluoranten, benzo(a)piren, dibenzo(a,h)antracen, benzo-(g,h,i)perylen i indeno(1,2,3-c, d)piren) zostały zbadane w próbkach w Wydziałowym Laboratorium Chemicznym Politechniki Białostockiej. W tym celu zastosowano metodę chromatografii gazowej sprzężonej ze spektrometrią mas przy użyciu chromatografu GC/MS Agilent 7890B. Wyniki podano jako pojedyncze związki WWA, które następnie pogrupowano według liczby pierścieni aromatycznych. Stwierdzono, że łączna zawartość 16 WWA zależy od rodzaju osadu ściekowego, przy czym najwyższa z nich występuje w osadach wstępnych, a znacznie niższa w innych osadach. Proces fermentacji i dalsze odwadnianie osadu fermentacyjnego zmniejszyły zawartość 16 WWA. Procesy transformacji wpłynęły na zawartość węglowodorów w poszczególnych grupach. Udział grup WWA w zależności od liczby pierścieni w sumie 16 zależał od terminu poboru badanych osadów. W badanych osadach dominowała grupa węglowodorów trój- i czteropierścieniowych, a najmniej dwu- i sześciopierścieniowych. Zawartość WWA we wszystkich analizowanych osadach nie przekraczała normy dla 11 WWA zaproponowanej przez Komisję Europejską dla osadów wykorzystywanych w rolnictwie.

Słowa kluczowe:
WWA, osady ściekowe, unieszkodliwianie osadów