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HEAVY METALS AND POLYCYCLIC AROMATIC HYDROCARBONS IN LEACHATES FROM AUTOTHERMAL THERMOPHILIC AEROBIC DIGESTION AS A POTENTIAL THREAT TO THE ENVIRONMENT IN NORTH-EASTERN POLAND

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Abstract:

This paper presents the concentrations of the polycyclic aromatic hydrocarbons (PAH) and heavy metals in leachates from the autothermal thermophilic aerobic digestion (ATAD). The leachates from ATAD installations (Dąbrowa Białostocka, Hajnówka, Pisz, Olecko, Giżycko, Wysokie Mazowieckie) located in Poland were tested. The concentrations of PAHs in samples from Pisz, Giżycko, Wysokie Mazowieckie and Hajnówka were similar to those in industrial wastewater. The cluster analysis confirmed that in sites with a higher polyethylene (p.e.) input from the industrial sector, the leachates were more contaminated with PAH compounds. In samples from Dąbrowa Białostocka, Olecko, Pisz and Hajnówka, the heavy fraction of PAHs compounds prevailed over the light fraction. Concentrations of heavy metals in leachates from ATAD varied. The Ward's method isolated the wastewater treatment plant in Giżycko. The p.e. from the industrial sector was the highest for this facility. Also, the samples from ATAD had the highest total concentration of heavy metals (5.87 mg/l). The leachates from ATAD are returned to biological systems of municipal sewage treatment plants, where they can be combined into more toxic compounds. Biological wastewater treatment processes do not ensure the removal of PAHs and heavy metals from the wastewater. As a result, harmful compounds can get into the water or ground, polluting the environment.

Key words: heavy metals, biodegradation, polycyclic aromatic hydrocarbons, leachates, autothermal thermophilic aerobic digestion.

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INTRODUCTION

According to the Central Statistical Office, the population served by wastewater treatment plants in Poland is steadily increasing. As a result, more and more municipal wastewater treatment facilities are being built. In 2009, there were 3153 wastewater treatment plants in Poland, whereas in 2019 there were 125 more (www.bdl.stat.gov.pl). For 5 years since 2010 the amount of sludge produced in municipal wastewater treatment plants in Poland has been constantly increasing. Since 2015, the number has remained at a similar but still high level.

In Poland and worldwide, legal requirements are established to treat sewage sludge before its natural use. Operators implement new solutions to improve sludge processing. Since 2003 in Poland, the autothermal thermophilic aerobic digestion (ATAD) installations started to be built (Bartkowska, 2017). At the moment, there are 11 ATAD installations in the country, located in the municipal wastewater treatment plants. Seven of them are in the northeastern part of the country. The ATAD installation enables simultaneous stabilization and hygienic treatment of sludge. It occupies a small area, the reactors are fully air tightened and the installed equipment allows to remove gaseous pollutants (Augustin *et al.*, 2007; Bartkowska, 2017). These are huge advantages improving technological processes in the treatment plants, but they exert negative effects in the environment. The leachates that are generated at the presses or centrifuges that dewater the sludge after ATAD, but also at the place where the air from the ATAD process is purified, scrubber the water (Hepner *et al.*, 2002; Bartkowska *et al.*, 2011).

The ATAD leachates have complex organic matter and contain large concentrations of the polycyclic aromatic hydrocarbons (PAH) compounds and heavy metals. The leachates are returned to the biological reactors of municipal sewage treatment plants. Various forms of polycyclic aromatic hydrocarbons are also present in municipal wastewater (Perez *et al.*, 2001; Włodarczyk-Makuła, 2005). PAH compounds are capable of combining with other matrix components (Włodarczyk-Makuła and Smol, 2011). Therefore, the combination of leachate from ATAD with municipal wastewater, can be expected to induce different transformations of PAH compounds, depending on environmental conditions. There is a possibility that more toxic derivatives will be formed due to ring bonding of PAHs.

Biological wastewater treatment can be ineffective because the leachate requiring treatment has a specific composition. PAH compounds are not easily biodegradable due to their hydrophobic properties and ease of absorption on particulate matter. This is especially true for hydrocarbons with more rings. Under anaerobic conditions, PAHs are degraded up to a hundred times slower (Włodarczyk-Makuła and Wierzbicka, 2013; Boruszko and Wojciula, 2020).

Municipal wastewater treatment plants are adapted to legal requirements, where nitrogen and phosphorus reduction is necessary, whereas in such plants the amounts of PAHs and heavy metals are not controlled (Journal of Laws of 2019, item 1311). Therefore, heavy metals as well as polycyclic aromatic hydrocarbons are delivered to the recipients.

The PAH are organic pollutants that occur naturally in many elements of the environment. However, due to anthropogenic activities, including the discharge of wastewater into receiving bodies, they begin to have highly toxic effects on plant and animal organisms (Włóka *et al.*, 2014; Teixeira *et al.*, 2015). As early as 1997, the PAH compounds were found to slow down or completely inhibit plant growth and development, and cause chronic leaf diseases (Smreczak, 1997). The PAH that enter the aquatic environment are carcinogenic and mutagenic (Hylland, 2006; Rengarajan *et al.*, 2015). They accumulate in aquatic living organisms, such as fish, which are then consumed by humans. Their toxicity causes many serious health ailments (Baumard *et al.*, 1998; Skupińska *et al.*, 2004). The PAH compounds having 4 or more rings are particularly dangerous. They have a high molecular weight, are resistant to decomposition and their half-life can be over 1800 years (Gateuillei *et al.*, 2014; Lamichhane *et al.*, 2016).

Heavy metals entering the receiving stream cause interference to many elements of the biocenosis and bioaccumulation in the food chain (Hławiczka, 2008). They accumulate in roots as well as in aboveground parts (Kabata-Pendias and Pendias, 1999; Gruca-Królikowska and Wacławek, 2006). They have the ability to penetrate biological membranes, disrupt photosynthetic processes, interfere with transpiration or cause increased oxidative stress in plants (Kaczyńska *et al.*, 2015). They can also reduce turgor in leaves or even disrupt RNA structure. Excess chromium can contribute to reduced plant uptake of needed micro- and macronutrients (Wolak *et al.*, 1999). Heavy metals entering the aquatic environment easily accumulate in bottom sediments and living organisms such as plankton and fish. Human consumption of contaminated fish causes numerous ailments such as kidney, liver, and heart damage, food poisoning, infertility and nervous system disorders (Ociepa-Kubicka and Ociepa, 2012; Szymonik and Lach, 2015).

In Poland and probably also in other countries of Europe, no studies related to the presence of PAHs and heavy metals in leachates from ATAD have been conducted. No action has been taken to analyse the problem of discharging treated wastewater (that has potentially elevated concentrations of PAHs and heavy metals due to the inflow of leachates from the ATAD) into the receiving. It is very important to analyse the problem, as more and more ATAD installations are likely to be built in Poland. It will result in discharging more and more complex PAH compounds with a large number of rings, toxic to living organisms. The aim of this study is to analyse the leachates from the ATAD plants in terms of their negative impact in the environment. The concentrations of PAHs and heavy metals in leachates from dewatering of sewage sludge stabilized by the ATAD method were evaluated.

MATERIALS AND METHODS

Leachates from six ATAD installations located in the Podlasie Voivodeship near municipal sewage treatment plants, were tested. Drainage devices such as presses, and centrifuges were the exact sampling sites. Therefore, the ready material for testing was the leachate from sewage sludge dewatering, which had previously been stabilized by the ATAD method. The facilities located in Dąbrowa Białostocka, Olecko, Pisz, Giżycko, Wysokie Mazowieckie and Hajnówka were selected.

The study was conducted from October to December 2019. During this period, 6 samples were obtained, one from each wastewater treatment plant. Each of these received samples was an averaging of samples obtained throughout the ATAD stabilized sludge dewatering cycle. The obtained finished ATAD samples were tested for PAH and heavy metal concentrations. The measurement was performed 3 times and the results were averaged. Sixteen PAHs (naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k) fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene), sum of PAHs and heavy metals were identified in the leachates.

In the PAHs content tests, gas chromatography combined with high identification capability of GC/MS Agilent 7890B mass spectrometry in DB-5MS column (Rice *et al.*, 2017) was used. The stationary phase of the column was made of polydimethylsiloxane with 5% phenyl groups. The PAHs extraction process was carried out in a liquid-liquid system at an ambient temperature of 20ºC. For the extraction of PAHs, 250 cm^3 of leachate sample was used, from which activated sludge was separated with a qualitative filter. Extraction was carried out with a mixture of dichloromethane and hexane in 2:1 volume ratio (50 cm^3 hexane and 100 cm^3 dichloromethane) on a magnetic stirrer at a speed of 600 RPM for 45 minutes. Then, the extract was separated from the leachate and concentrated to a volume of 1.5 cm^3 using a laboratory evaporator at a vacuum of 280.0 mbar and a temperature of 35ºC. The prepared sample was subjected to quantitative analysis.

Six solutions containing a standard calibration mixture and a matrix of the tested sample were analysed. The calibration function was calculated by means of linear regression of corrected peak areas. The current sensitivity of the method was estimated based on the calculated regression function. The calibration was performed on the day of measurement. A certified reference material was also determined for PAHs recovery. The values of recovered PAHs ranged from 85% to 110%, which is acceptable for chromatographic methods (Oleszczuk and Baran, 2004). The detection limit was 10 $ng*kg^{-1}$ of dry matter. The accuracy expressed as relative standard deviation was below 12%.

In order to determine heavy metals, leachates samples were mineralized in the Milestone mineralizer in aqua regia (a mixture of nitric and hydrochloric acid). For further analysis, the samples were filtered through an MN 616 G paper filter. Determination of heavy metals content was performed on inductively coupled plasma mass spectrometer (ICP/MS Agilent 8800). Determination of tested samples was performed in three repetitions.

Statistical analysis of the study results consisted of a cluster analysis using the Ward's method with Euclidean distance (Siegel, 1956; Sobczyk, 2011). Its purpose was to determine groups of wastewater treatment plants similar in terms of PAH concentrations and a higher p.e. for industrial wastewater.

RESULTS AND DISCUSSION

The conducted research allowed to conclude that leachates from sludge dewatering after ATAD stabilization contains heavy metals as well as polycyclic aromatic hydrocarbons, including the most harmful ones, considered as priority hazardous substances in the field of water policy (Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000). Table 1 shows the average PAHs concentrations in the leachates samples after ATAD for each selected wastewater treatment plant.

Polycyclic aromatic hydrocarbons were found in each analysed sample (Table 1). The least PAHs concentrations were found in leachates from the treatment plant in Olecko (2.89 µg/l) and the most in Hajnówka (56.65 µg/l). The difference was about 95%. A high benzo(b)fluoranthene concentration of 14.98 µg/l was found in Hajnówka. In the remaining samples the amount of this compound was within 1 µg/l. A similar relationship was found for indeno(1,2,3-cd)pyrene. In the leachate from the Hajnówka, the concentration of indeno(1,2,3-cd)pyrene was 22,88 µg/l, and in samples from other treatment plants, the compound was 20 times less. So far, no studies related to the presence of PAHs in leachates from ATAD have been conducted. The authors present only the concentrations of these compounds in municipal, domestic, and industrial wastewater. For example, Włodarczyk-Makuła and Smol (2011) showed the presence of benzo(k)fluoranthene in the amount of 3.22 µg/l in coke-oven wastewater. For comparison, 3.47 µg/l of benzo(k)fluoranthene occurred in the leachates after the ATAD from Hajnówka. The authors also reported a benzo(g,h,i)terylene concentration of 1.93 µg/l in the coke oven

Table 1. Average PAHs concentrations in samples of ATAD leachates from selected sewage treatment plants.

Chemical compound	Average PAHs concentration [µg/l]					
	Dąbrowa Białostocka	Olecko	Pisz	Giżycko	Wysokie Mazowieckie	Hajnówka
Naphthalene	0.425	0.431	1.054	0.815	5.02	1.434
Acenaphthylene	0.015	0.027	0.024	11.452	2.474	0.148
Acenaphthene	0.089	0.581	0.696	1.157	3.114	4.465
Fluorine	0.013	0.022	0.052	0.087	0.191	0.043
Phenanthrene	0.022	0.022	0.187	0.205	0.323	0.468
Anthracene	0.005	0.008	0.013	0.119	0.043	0.6
Fluoranthene	0.009	0.016	0.107	0.407	0.468	0.3
Pyrene	0.004	0.017	0.003	0.323	0.438	0.326
Benzo(a)anthracene	0.047	0.008	0.028	0.277	0.181	0.441
Chrysene	0.005	0.017	0.052	0.397	0.248	1.594
Benzo(b)fluoranthene	0.195	0.389	0.729	1.674	0.488	14.982
Benzo(k)fluoranthene	0.133	0.089	0.168	0.268	0.087	3.466
Benzo(a)pyrene	0.233	0.063	0.144	0.582	0.146	1.262
Dibenzo(a,h)anthracene	1.28	0.019	0.017	0.684	0.773	1.422
Indeno(1,2,3-cd)pyrene	0.378	0.175	1.619	1.224	0.226	22.876
Benzo(g,h,i)perylene	2.279	1.01	3.06	2.218	1.134	2.819
Sum of PAHs	5.132	2.894	7.954	21.889	15.356	56.648

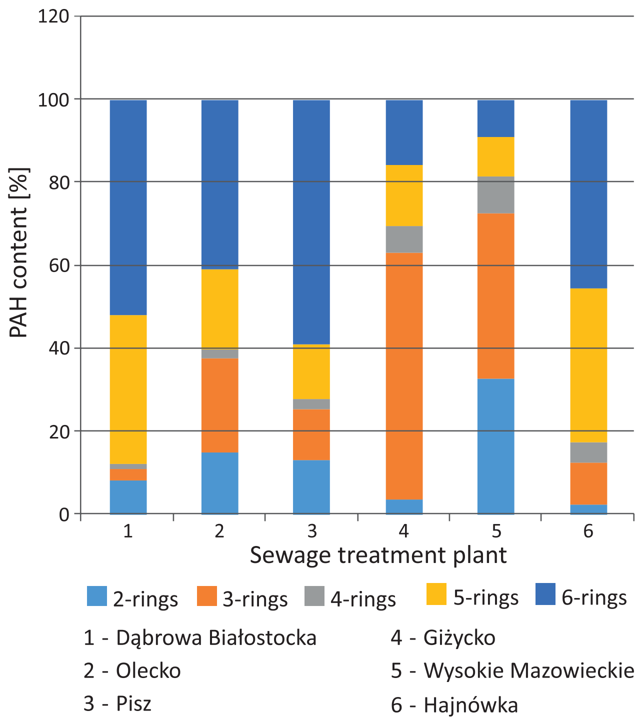

Fig. 1. Percentage share of 2, 3, 4, 5 and 6-ring PAHs in relation to the sum of 16 PAHs (100%) in the ATAD leachates from selected wastewater treatment plants.

wastewater. In 4 of the 6 analysed leachates after ATAD, higher concentrations of this compound were shown.

Figure 1 shows the percentage share of 2, 3, 4, 5 and 6-ring PAHs in total 16 PAHs in the ATAD leachates from selected wastewater treatment plants. 6-ring hydrocarbons predominated in leachates from Dąbrowa Białostocka, Olecko, Pisz and Hajnówka. Their amount oscillated in the range of 40–60% in relation to the sum of PAHs.

The smallest share in the total concentration of PAH compounds was found in 4-ring hydrocarbons and it was from 1 to 9%. An exception was the sewage treatment plants in Giżycko and Hajnówka, where the least number of 2-ring compounds (naphthalene) was found. The values of the remaining hydrocarbons were varied. Macherzyński *et al.* (2012) presented concentrations of 16 most harmful PAHs in leachate from the tank used for cooling and purifying coke-oven gas. According to the authors, the 2-ring compound (naphthalene) had the largest share in the total content of 16 PAHs and it was 38%. 30% constituted 3-ring compounds. The least 6-ringed PAH compounds were found. Their amount did not exceed 4% of the total concentration of 16 PAHs. The results presented by the authors significantly differed from those obtained in leachates studies after ATAD. The leachates from ATAD contained much higher concentrations of the most complex and simultaneously the most difficult to decompose PAH compounds. Also 5-ring hydrocarbons were found in higher concentrations in leachates from the ATAD than in leachate from the coke industry. This group includes benzo(a)pyrene, the most toxic compound of all PAHs.

The PAHs can also be divided into light and heavy fractions. This is determined by the molecular weight, i.e., the number of rings they are made of LMW, a light fraction of PAH, contains hydrocarbons consisting of 2 and 3 aromatic rings. HMW, a heavy fraction of PAH, are compounds with 4 and more rings (Lamichhane *et al*., 2016). It is important to analyse the PAHs in terms of fractions, because the greater the number of rings, the longer half the hydrocarbon degradation time (Banach-Szott *et al*., 2012). In addition, the PAH compounds with a smaller number of rings have a much higher solubility in water than compounds with a larger number of rings (Tian *et al*. 2012; Biache *et al.*, 2014; Yaws, 2015). Figure 2 shows the PAH content divided into light and heavy fractions.

According to Figure 2, the leachates from Dąbrowa Białostocka, Olecko, Pisz and Hajnówka were dominated by the heavy fraction of PAHs. The highest proportion of HMW PAH was found in the leachates from Dąbrowa Białostocka (88.9%) and Hajnówka (87.4%). This means that more complicated PAH compounds with more rings are returned to biological sewage treatment plant systems. Of course, the HMW PAH fraction can be decomposed under the conditions of biological wastewater treatment involving microorganisms, but this is difficult and requires the creation of appropriate conditions. For example, benzo(a)pyrene can be decomposed by aerobic bacteria of the genus *Bacillus*, but only in the presence of the cubstratum. On the other hand, there are studies confirming that the additive in the form of a compound caused a complete inhibition of PAHs biodegradation (Kwapisz, 2006; Włodarczyk-Makuła and Wiśniowska, 2018). It should be

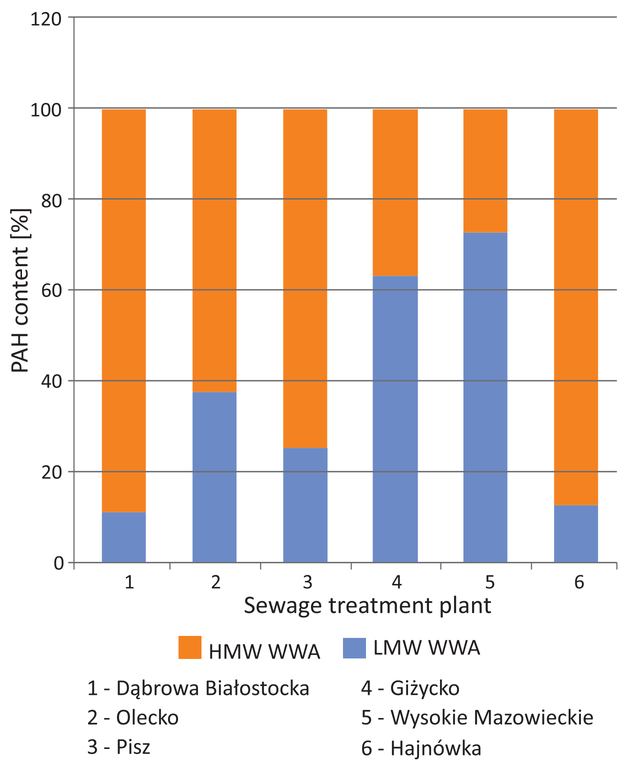

Fig. 2. Percentage content of the PAHs fractions in the ATAD leachates in selected sewage treatment plants.

noted that benzo(a)pyrene is the most mutagenic hydrocarbon (Sapota, 2002; Mazur-Badura, 2010). Therefore, in order to effectively biodegrade PAHs, it is necessary to know the tested environment, select the correct strains of bacteria and ensure other important physicochemical conditions (temperature, reaction, other matrix components). This practice is not applied in municipal wastewater treatment plants as legal requirements do not take into account the removal of PAHs from municipal wastewater. Therefore, it is dangerous to return ATAD leachates to biological wastewater treatment systems. In samples from Giżycko and Wysokie Mazowieckie the LMW fraction was <60% and <70%, respectively. Such a situation may also pose a certain risk, because the PAH compounds are able to combine with other matrix components (Włodarczyk-Makuła and Smol, 2011), i.e. after combining the leachate with municipal sewage, more complex hydrocarbons are likely to be formed. Heavy fractions of PAHs accumulate in the environment for many years and pose a huge threat to fauna and flora (Ikenaka *et al.*, 2013). Polycyclic aromatic hydrocarbons have affinity for lipids and therefore easily accumulate in fatty tissues. Living aquatic organisms are exposed to PAHs in water and bottom sediments (Noaksson *et al.*, 2003; Stołyhwo and Sikorski, 2005). People, in turn, by eating contaminated fish and seafood, unwittingly introduce toxic compounds into the body. The PAHs are mutagenic and carcinogenic. They also show immunotoxic effects. Excess hydrocarbons contribute to changes in the bone marrow, lymph nodes or thymus. Apart from many other ailments, these compounds disturb the maturation process of cells as early as at the stage of fetal life (Zasadowski and Wysocki, 2002).

As a result of agglomeration of variables by the Ward's method, the classification tree shown in Figure 3 was obtained. In order to perform the analysis, variables characterizing the selected wastewater treatment plants were taken. The first variable is the total PAHs concentration and the second is the p.e. for industrial wastewater. The value of p.e. for industrial wastewater was calculated based on data from the Central Statistical Office (bdl.stat.gov.pl). This allowed us to determine which facilities receive the most industrial wastewater.

As shown in Figure 3, cluster analysis identified two groups of dependent variables. The first concerns the wastewater treatment plants in Olecko, Wysokie Mazowieckie, Pisz and Dąbrowa Białostocka, and the second – the wastewater treatment plants in Giżycko and Hajnówka.

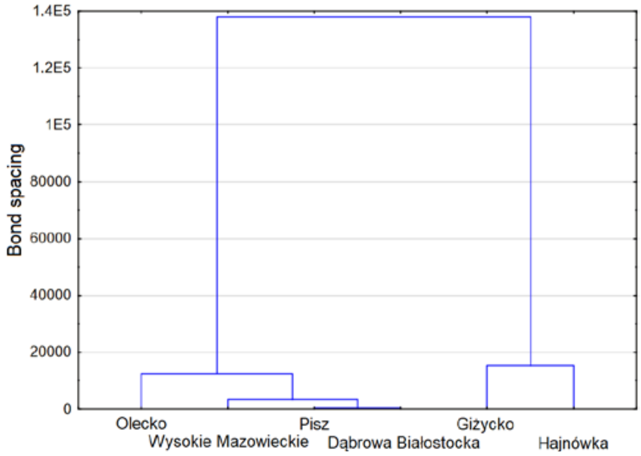

Fig. 3. Dendrogram of cluster analysis conducted by the Ward's method.

The first group presents sites from which leachates after the ATAD contain lower concentrations of the PAHs and lower p.e. from the industrial sector than the leachates from the sites of the second group. In Dąbrowa Białostocka and Pisz there are no major industrial facilities, while in Olecko and Wysokie Mazowieckie there is one plant producing dairy wastewater.

The second group specifies wastewater treatment plants from which the leachates after the ATAD contain the highest concentrations of the PAHs. At the same time, these plants receive large amounts of industrial wastewater. In Giżycko, the communal treatment plant receives dairy sewage. Besides, there is a production of electrical switchboards and a production of boilers and pellet burners in the town. In Hajnówka the source of industrial wastewater is the Branded Brewery as well as the District Dairy Cooperative located in the town. Along with industrial wastewater, municipal wastewater treatment plants receive high concentrations of the PAH compounds.

Table 2 shows concentrations of heavy metals in the leachates after the ATAD process from selected wastewater treatment plants. The heaviest metals were found in the

Table 2. Heavy metal concentrations in leachates after the ATAD.

Trace element	Medium content of heavy metals [mg/l]					
	Dąbrowa Białostocka	Olecko	Pisz	Giżycko	Wysokie Mazowieckie	Hajnówka
Cr	0.013	0.009	0.06	0.025	0.011	0.002
Pb	1.952	0.835	0.992	5.107	3.717	0.298
Cd	0.012	0.033	0.023	0.086	0.138	0.007
Ni	0.007	0.014	0.067	0.071	0.012	0.003
Cu	0.014	0.066	0.377	0.187	0.028	0.052
Zn	0.097	0.391	1.89	0.392	0.158	0.175
Hg	nd	0.001	0.004	0.003	0.003	nd
Sum of metals	2.095	1.349	3.413	5.871	4.067	0.537

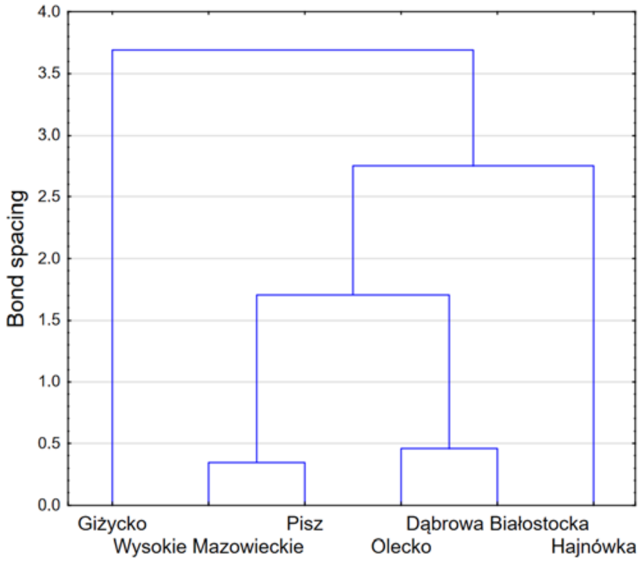

Fig. 4. Dendrogram of cluster analysis conducted by the Ward's method.

leachate from Giżycko (Fig. 4). This result was influenced by the concentration of lead, which was 5.11 mg/l. For comparison, 17 times less of this metal (0.30 mg/l) occurred in the leachate from Hajnówka. The likely cause of lead contamination of the Giżycko leachate is the presence of the District Dairy Cooperative in Giżycko, from which wastewater is discharged to the municipal treatment plant. The least heavy metals were found in the leachate from Hajnówka. Their sum was 0.537 mg/l. In comparison to all tested samples, the highest concentration of chromium was found in the leachate from Pisz (0.06%). In the case of cadmium, a high concentration was detected in the sample from Wysokie Mazowieckie (0.138 mg/l). The highest concentration of nickel was found in the leachate from Giżycko, while the leachate from Pisz showed the most copper, zinc and mercury.

The cluster analysis conducted allowed us to distinguish three groups of dependent variables (Fig. 4). The first group presents the facility from which the leachates after ATAD contain the highest total concentration of heavy metals. At the same time, it is the treatment plant that receives the largest amount of industrial wastewater. These are mainly wastewater from a dairy plant, as well as from a boiler and burner manufacturing plant. It is likely that the wastewater from the second facility contained a significant concentration of lead, which contributed to the high total heavy metal content. A separate group is the sewage treatment plant in Hajnówka, which also receives a relatively large amount of dairy and brewery wastewater. However, significantly lower amounts of metals were found in this locality than in the samples from Giżycko. The reason for this may be that the District Dairy Cooperative in Hajnówka has the most modern technological lines that meet requirements of the European Union (Struk-Sokołowska and Ignatowicz, 2013). The third group presents treatment plants in Wysokie Mazowieckie, Pisz, Olecko and Dąbrowa Białostocka. The p.e. ratio for industrial wastewater at these facilities was lower than at the others and the total amount of heavy metals in each sample was lower than in the leachate from Giżycko. There are no major industrial facilities in Dąbrowa Białostocka and Pisz, while there is one plant producing dairy wastewater in Olecko and Wysokie Mazowieckie.

To date, there have been no studies representing heavy metal concentrations in leachates after the ATAD process. As in the case of the PAH compounds, municipal treatment plants are not obliged to remove heavy metals from wastewater. Therefore, the elements end up together with wastewater in water or soil, polluting the environment. Heavy metals have the ability to migrate, especially in acidic environments. They can penetrate the biological membranes of plants and their interference results in changes in physiological processes and even in the genetic code (Cheng, 2003; Filipek, 2003; Ociepa *et al.*, 2014). Heavy metals easily bioaccumulate in living organisms. They can be directly transferred from the aquatic environment to fish and seafood. In turn, by consuming these products, human assimilates trace elements. Cadmium, zinc, lead, or mercury cause both chronic negative health symptoms and immediate acute poisoning (Godt *et al.*, 2006). They can contribute to changes in human genetic material and lead to diseases of the nervous, digestive and circulatory systems. Cadmium is particularly dangerous because its biological half-life can reach 30 years. It accumulates in tissues for a long time and above all, it accumulates in the parenchymal organs such as liver, pancreas or kidneys (Kabata-Pendias and Szteke, 2000; Ociepa-Kubicka and Ociepa, 2012).

CONCLUSIONS

Summarizing the results and findings, the following conclusions can be formulated:

- Heavy metals and polycyclic aromatic hydrocarbons were found in the leachates from the ATAD process. The concentration of PAHs in four samples was similar to the concentration of these compounds in industrial wastewater. The PAHs concentration in all samples was higher than those in raw municipal wastewater.
- The heavy fraction of the PAH compounds predominated in samples from the treatment plants in Dąbrowa Białostocka, Olecko, Pisz and Hajnówka over the light fraction. This means that more PAHs with at least 4 rings are released into the environment. This is dangerous for the environment, because hydrocarbons with a large number of rings decompose much worse in water and their half-life can be up to 1800 years.
- The highest concentration of the sum of 16 PAHs, amounting to 56.65 μg/l, was found in the ATAD leachate from the sewage treatment plant in Hajnówka, and the lowest, amounting to 2.89 μg/l, was found in the ATAD leachate from the sewage treatment plant in Olecko. The likely reason is the presence of more industrial plants in Hajnówka than in Olecko.

- The most toxic compound of the PAH group, benzo(a) pyrene, was found at the highest concentration of 0.58 μg/l in the leachate from Giżycko and at the lowest concentration of 0.063 μg/l in the leachate from Olecko.
- The share of 6-ring aromatic hydrocarbons in relation to the sum of 16 PAHs was much higher in the leachates from the ATAD (except for the leachate from Wysokie Mazowieckie) than in the leachates from the tank used for cooling and purifying coke oven gas.
- Most heavy metals were found in the leachates from Giżycko. The greatest influence was exerted by the lead concentration, which amounted to 5.11 mg/l. In the leachate from Hajnówka 17 times less of this metal occurred (0.30 mg/l). The probable reason for the high concentration of lead in the Giżycko leachate is the presence of the District Dairy Cooperative in Giżycko, from which the wastewater flows into the municipal treatment plant.
- Cluster analysis, in which one of the variables was the concentration of the PAHs in leachates, identified two groups of wastewater treatment plants. Wastewater treatment plants in Hajnówka and Giżycko were separated as one group, because the ATAD leachates from these plants showed high concentrations of PAHs, determined by the large inflow of industrial wastewater.
- The ATAD leachates are returned to biological systems, where they can combine into more complex toxic compounds. Wastewater treatment processes in municipal wastewater treatment plants are not adapted to remove PAHs, as it is not required by law. Therefore, the complicated, specific PAH compounds are deposited in the wastewater receivers, polluting the environment.

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