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Accumulation of PAHs in plants from vertical flow-constructed wetland

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ABSTRACT

The aim of the investigation was to determine PAHs concentration in the biofilter and in parts of the plant taken from a wetland wastewater treatment plant vertical flow-constructed wetland in technical conditions. Determination of PAHs in parts of plants of *Glyceria maxima*: roots, stems, and leaves was carried out. The high pressure liquid chromatography with a diode array detector was used for qualification and quantification of PAHs. The extraction process for samples was carried out in an ultrasonic bath with dichloromethane as solvents. Then extracts were purified using SPE columns packed with silica gel in vacuum conditions. The 16 PAHs according to US EPA list were analyzed. The initial contents of total PAHs were 37 μg/kg dm on average. Concentration of these compounds in roots was twice as high (85 μg/kg dm). The highest concentration of analyzed hydrocarbons in leaves was noted (143 μg/kg dm). In extracts from the surface of leaves the total of PAHs concentration did not exceed 60 μg/kg dm. It demonstrates the ability of deposition of these compounds from the air. The content of PAHs in stems (92 μg/kg dm) was similar to the content of these compounds in roots (85 μg/kg dm).

Keywords: Wastewater; VF-CW treatment plant; PAHs; HPLC-DAD

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1. Introduction

Rural settlements in Poland are dispersed. There are about 53,000, including 43.8 thousand villages, 10.2 thousand hamlets, and other populated places in the country. The population density in these places is varied: in a number of them it does not exceed 100 people, and the average is 277 inhabitants per settlement. The high dispersion of settlements makes water and sewage management difficult. This is especially a problem in the case of sewer systems and sewage treatment plants. Consequently, there is a need for more investments, and high operational costs of communal infrastructure, especially sewer systems [1].

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There are two types of system solutions to the problem of sewage disposal and sewage treatment. One is a sewer network with a group sewage treatment plant. In this case, it is necessary to build extensive sewer networks over a vast area and transport sewage to a common sewage treatment plant. The other solution is to build individual sewage treatment systems (household sewage treatment plants), which are better in terms of investment attractiveness.

Among technological solutions for household sewage treatment plants, wetlands systems are becoming more and more popular in Poland. These sewage treatment plants reflect natural hydraulic and habitat conditions of marsh ecosystems. In natural environment, such a system is a natural wetland throughout most of the year, where the constant presence of water causes the growth of typical marsh and water plants (hydrophytes). The method of wetlands sewage treatment with the use of plants consists in the biochemical degradation of organic and biogenic compounds with the participation of heterotrophic micro-organisms. A group of these micro-organisms, including different species, is immobilized in the bed. This is filled with minerals (less often organic matter), and artificially populated with hydrophytes [2]. Depending on the direction of the sewage flow, there are free water surface or surface flow systems and vegetated submerged beds (VSB) or subsurface flow systems. In the VSB system there are two types: horizontal flow-constructed wetland (HF-CW) and vertical flow-constructed wetland (VF-CW).

The main processes occurring in wetlands sewage treatment plants are: adsorption, biochemical oxidation–reduction reactions, ion exchange, sedimentation, and evapotranspiration. The mineralization of organic substances, nitrification, denitrification, or dephosphatation processes mainly occur with the participation of soil micro-organisms [3]. The processes of biological activity of plants mostly depend on the type of vegetation, the range of the root system, the type of bed and its porosity, hydraulic conditions, and the size of the bed. The mechanisms of pollution removal in wetlands sewage treatment plants are presented in Fig. 1. A characteristic feature of wetlands sewage treatment plants is the, so-called, rhizosphere effect. Macrophytic plants, due to air-filled tissue—aerenchyma, can transport oxygen from the air to the rhizosphere. An oxygen-filled zone is formed in the closest vicinity of the roots, and further away from the roots and rootstocks there is an anaerobic zone. Thus, a mosaic of aerobic and anaerobic zones is formed, called a rhizosphere, which provides the right conditions for the metabolism of different organisms [4].

The effectiveness of the removal of pollution occurring in the form of total suspended solids and organic compounds, expressed by the indexes BOD_5 and COD (especially in HF-CW systems) is very well documented in literature [6–9]. Twenty years' experience in the use of these systems has proven that their effectiveness at removing total suspensions is over 90% [10], at decreasing the BOD_5 index in sewage—98% [11], and at decreasing the COD index—up to 90%. The effectiveness of removing biogenic compounds in wetland sewage treatment plants can be varied. According to literature, the effectiveness of removing nitrogen compounds from sewage is between 10 to 70% [12,13].

There is a similar lack of precision about the removal of phosphorus. Literature data indicate that this effectiveness is between 11 and 94% [14,15]. The research carried out by Puigagut in Spain, in wetland sewage treatment plants built at the beginning of the 21st century, which operated as HF-CW and VF-CW systems, showed that the effectiveness of removing organic substances expressed as BOD_5 was 80% in the HF-CW system and 95% in the VF-CW system. The effectiveness of removing biogenic compounds was considerably lower. It was 50% for total nitrogen, and it did not exceed 40% for ammonia nitrogen and total phosphorus [16].

According to literature, the effectiveness of removing pollution (mainly biogenic) is determined by climate conditions. Mæhluman and Jenssen [17] indicated that the height of 0.9 m is sufficient to protect the bed from freezing and to keep the sewage in the bed for a sufficient time. The results of monitoring wetland sewage treatment plants in Norway confirmed their high effectiveness at removing organic pollution, which was 67–90% for the BOD_5 index, and 41–88% for the COD index. The removal of total phosphorus was varied and ranged from 26 to 98%, and total nitrogen from 55 to 80%. The research results led to the conclusion that in HF-CW systems, the sewage retention time had a considerable impact on the effectiveness of the sewage treatment plant. Better effectiveness at removing pollution was observed when the retention time was 15–30 d in comparison to 12–14 d [18–21].

The requirements for the quality of sewage treatment in Poland are specified by the applicable legal regulations [22]. In relation to household sewage, similarly to the EU regulations, the acceptable values are specified for five indexes. They are indexes of organic pollution: BOD_5, COD, total suspensions, total nitrogen, and total phosphorus. The highest acceptable values of the abovementioned indexes depend on the

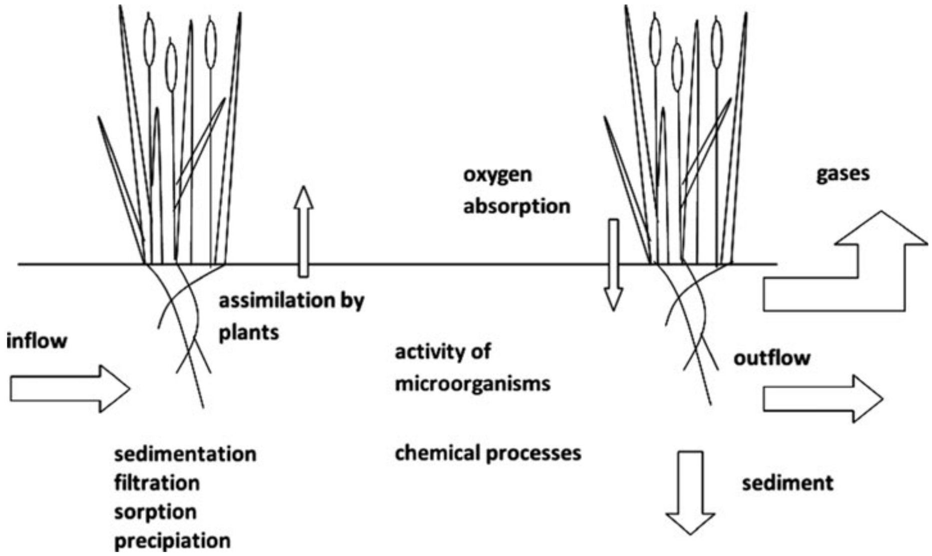


Fig. 1. The mechanisms of pollution removal in wetlands sewage treatment plants [5].

amount of PE (population equivalent) and are specified for sewage coming out of municipal sewage treatment plants. As far as individual systems are concerned, with reference to sewage coming from households and passing into the ground right where it is produced, only one requirement has been specified—the value of the BOD_5 index has to be lowered by 20% in sewage coming into the sewage treatment plant and total suspensions have to be reduced by 50%. A review of the legal regulations indicates that they do not specify the acceptable PAH concentrations in sewage passed into collection reservoirs. However, there is a directive with a general requirement that certain chemical compounds should be eliminated from sewage because of their carcinogenicity [22]. Polycyclic aromatic hydrocarbons can be included into this group because toxicological examination has often confirmed that they have carcinogenic, mutagenic, and teratogenic effects on bioindicators. From among 16 compounds selected by the American Agency for Environmental Protection, eight are toxic to organisms [23]. The International agency for Research on Cancer also included them on the list of substances that might have carcinogenic effects on humans (group 2B according to IARC) [24]. In spite of the lack of requirements for monitoring PAHs in purified sewage passing into collection reservoirs, they are mentioned in the legal regulations on monitoring surface and underground waters, as well as among the priority substances for the water environment [25,26]. Taking into account the toxic characteristics of PAHs, and the lack of information in literature about PAHs in individual wetland sewage treatment plants, an investigation was started to determine the quantity of PAHs in a particular object. The goal of the investigation was to determine the PAH concentration in the biofilter and in samples of plants taken from a VF-CW sewage treatment plant in technical conditions.

2. Materials and metods

2.1. Vertical flow-constructed wetland

The subject of the research was a *wetland* sewage treatment plant operating as a VF-CW. The plant is located in the south of Poland. It started working in 2009. A general technological scheme of the sewage treatment plant is shown in Fig. 2, and a view of the plant in Figs. 3 and 4. The average daily output of the plant is $Q_d = 0.5\ m^3/d$. The purified sewage passes into the ground through the effluent polishing pond. The sewage treatment plant consists of four components:

(1) the one-chamber septic tank with the capacity of $V = 4\ m^3$;
(2) the sewage pumping station built of concrete rings with the capacity of $V = 0.8\ m^3$;
(3) the bed surrounded with earth dykes with the dimensions 3.0×3.5 and area $10.5\ m^2$;
(4) the effluent polishing pond with an irregular shape and the area $15\ m^2$.

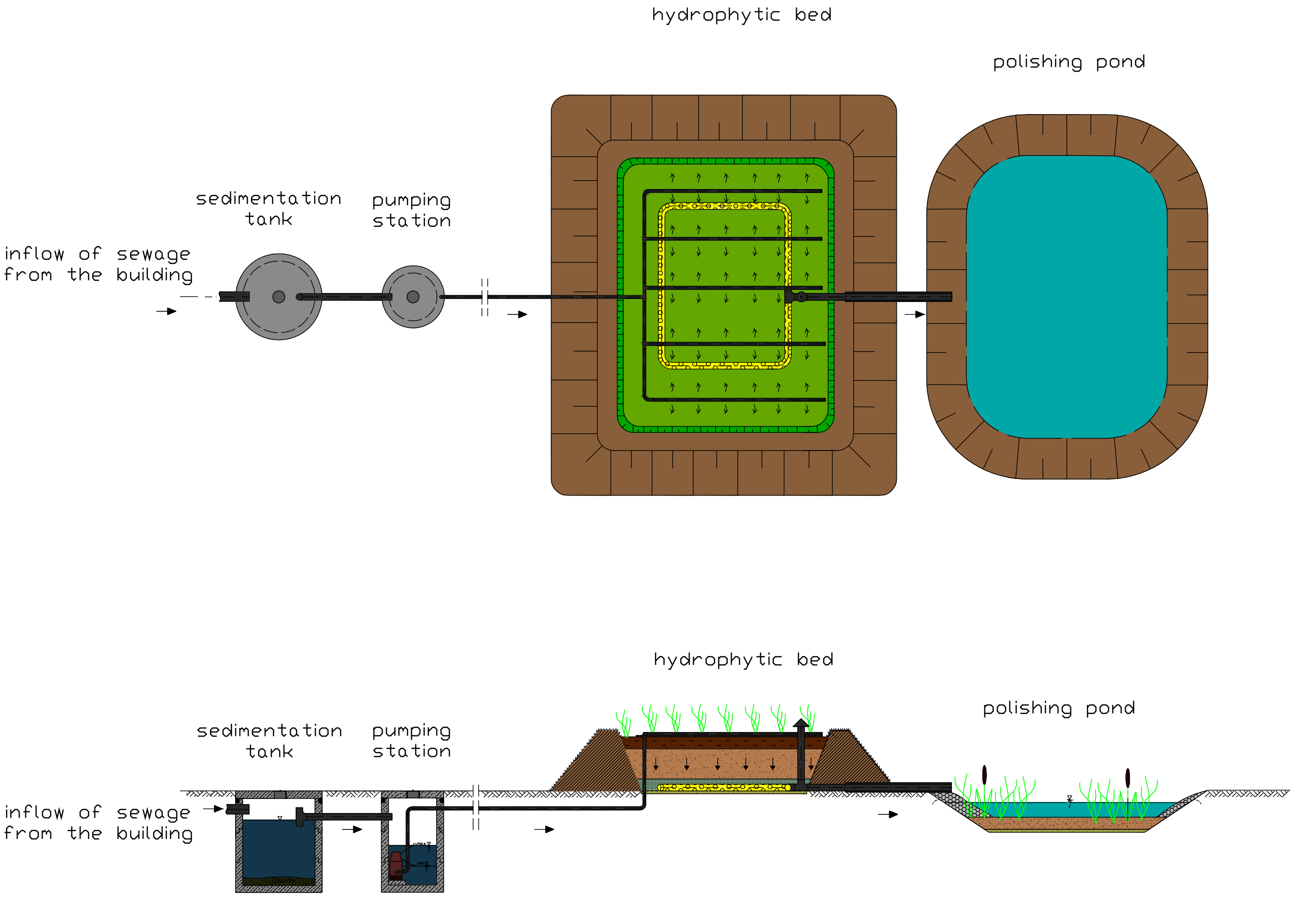


Fig. 2. The technological scheme of the VF–CW [27].

Fig. 3. A view of the hydrophytic bed (photo: author).

Fig. 4. A view of the effluent polishing pond (photo: author).

Initial mechanical purification takes place in the sedimentation tank. This is a monolithic structure of reinforced concrete. Another component of the sewage treatment plant is the sewage pumping station, which pumps the sewage into the VF plant filter media. A third component of the sewage treatment plant is the three layer plant filter media with the thickness of 1.0 m. This is isolated from the subsoil with a PE geomembrane with the thickness of 1 mm. The first layer from the bottom consists of gravel ($\Phi = 4–32$ mm), the next layer consists of medium sand ($\Phi = 0.5–2$ mm), and the final layer consists of a mixture of tree bark, sawdust, and woodchips. The area of the bed is 2 m^2/M as specified in Patent No. 198680 [27]. The bed area is planted with reed mannagrass (*Glyceria maxima*) and upright sedges (*Carex elata*). The final component of the sewage treatment plant is the effluent polishing pond, located at the depth of 0.7 m and partially isolated from the subsoil with a PE geomembrane with the thickness of 1 mm. The effluent polishing pond is planted with macrophytic plants: narrowleaf cattails (*Typha angustifolia*) and broadleaf cattails (*Typha latifolia*). The purified sewage passes into the subsoil through the surrounding escarpment, which is covered with medium sand ($\Phi = 0.5–2$ mm), with an additional mixture of metal chips.

The basic physical and chemical indexes were marked in the raw and purified sewage:

1. Chemical demand for oxygen, COD according to PN-ISO 6060:2006;
2. Biochemical demand for oxygen, BOD_5 measured with an OxiTop Control OC110 set according to PN-EN 1899–1:2002;
3. Ammonia nitrogen in a Vapodest 30 device according to PN-C-04576-4:1994;
4. Nitrate nitrogen—According to PN-82 C-04576.08;
5. Total nitrogen—In a Vapodest 30 device according to PN-EN 25663:2001;
6. Total phosphorus—Measured with a Marcel Media spectrophotometer according to PN-EN ISO 6878:2006.

2.2. Experimental procedure

Samples of biofilter as well as parts of plants were collected in autumn after 4 years of exploitation of that experimental plot. The samples of biofilter were taken from the depth of 0–20 cm; individual samples were taken once from six points regularly disposed on an experimental plot area. All samples which were taken from the plot were mixed to obtain representative samples. Air dried samples were sieved through a sieve with the mesh diameter of 1 mm. Whole, healthy plants were dug in order to collect some part of plants. Plants were divided into roots, stems, and leaves. Leaves were collected by picking several leaves with petioles at the height of about half of the willow corona. Stems were taken from a half of three heights. Roots samples were of 10 cm length. Plant samples were left in a canopied chamber at room temperature to dry. Air dried parts of plants (roots and stems) were mechanically ground to obtain woodchips. Two samples leaves were prepared: one in a mortar were ground, second sample with solvents were flooded.

2.3. PAHs analysis

The high pressure liquid chromatography with a diode array detector (HPLC-DAD) was used for PAHs qualification and quantification. Extraction of the samples was carried out in an ultrasonic bath with cyclohexane and dichloromethane mixtures as solvents. Prepared extracts were primarily concentrated under a nitrogen stream to a volume of 3 mL. Then those extracts were purified using SPE columns packed with silica gel in vacuum conditions. Subsequently, extracts were concentrated again to a dry residue. Dry residue was then diluted in acetonitrile and used for chromatographic analysis. PAHs were qualified and quantified with a high-performance liquid chromatography method with a fluorometric detector. Identification of individual compounds was realized based on retention times of the compounds with retention times of standard solutions.

HPLC chromatograph Waters model Alliance 2,695 with Supelcosil LC-PAH column (15 cm × 4.6 mm × 5 μm) was used. A fluorometric detector waters 2,475 and a photoindicator detector waters 2,998 were used. The parameters of the instrumental method were as follows: time of analysis 40 min, time of stabilization 8 min. Flow velocity through the column was equal to 1.5 mL/min, temperature of column thermostating 25°C. The fluorometric detector worked at wavelength of induction (extraction WL) equal to 275 nm and wavelength of emission (emission WL) equal to 350 nm.

To verify the method of samples' preparation for qualification and quantification of PAHs, some control samples with known concentration of PAH compounds were prepared. A standard mixture of PAHs (Accu Standard Inc. USA—PAH Mix) in benzene and dichloromethane (v/v 1:1) was spiked into soil amended with sewage sludge and into plant samples. The standard mixture was added to samples before adding the solvents and before they were extracted. Afterward, the samples were carefully mixed, extracted and analyzed for PAHs according to the procedure described above. The recoveries of PAHs standard mixture for concentrations in samples varied from 77 to 103%. The average value was 85% which corresponds to the data found in the literature [28–30]. All analyses were done in triplicate. The following compounds were analyzed: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(j) fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah)anthracene, benzo (ghi)perylene, and indeno(1,2,3,c,d)pyrene. In Fig. 5, the chromatogram of samples is presented.

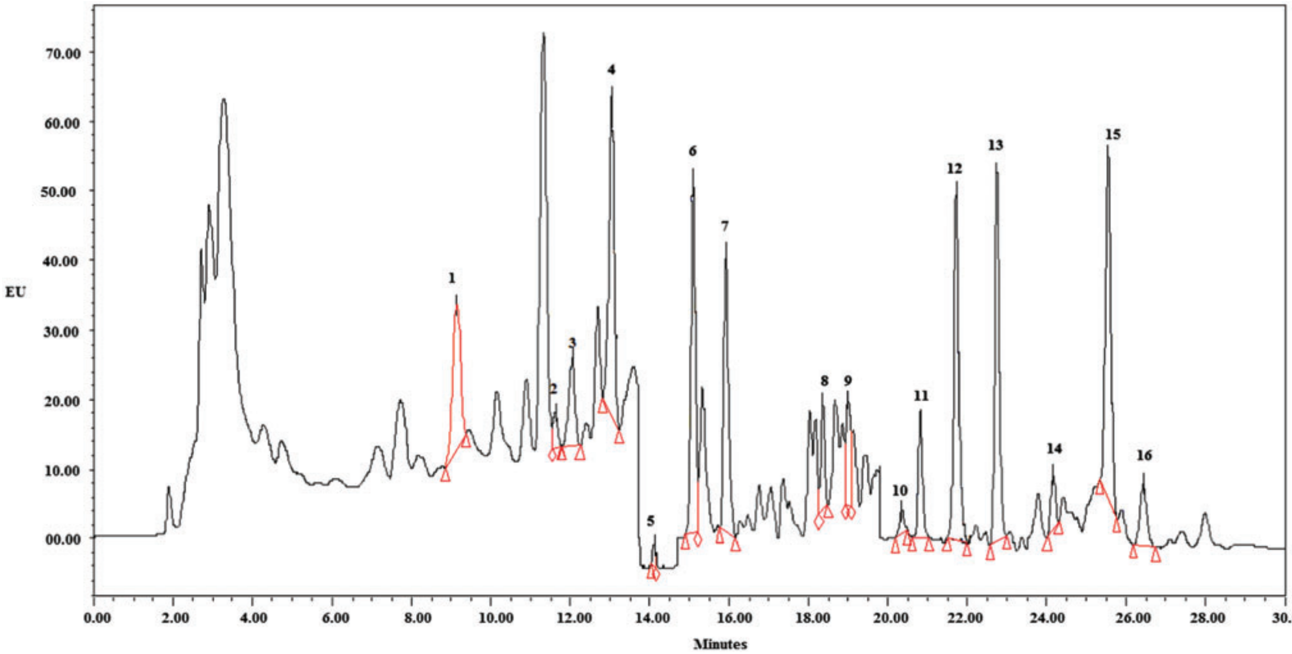
3. Results

3.1. Results of the physical and chemical analysis

Table 1 presents the characteristics of the raw wastewater and purified wastewater in the plant under examination. The raw wastewater in the research period had BOD_5 from 188 to 311 mg O_2/L, and COD from 388 to 472 mg O_2/L. The average value of the ammonia nitrogen was 71 mg/L, nitrite nitrogen—1.06 mg/L, and total nitrogen—86 mg/L. The average concentration of total phosphorus was 12.04 mg/L. In the purified wastewater, the average concentration of ammonia nitrogen was 8.82 mg/L, nitrate nitrogen 16.44 mg/L, and total nitrogen 27.68 mg/L. The average concentration of total phosphorus was 1.94 mg/L. The efficiency of removing organic pollution was high. For BOD_5 it was from 86 to 96%, and for COD from 85 to 93%. In the sewage treatment plant under examination, the on-going process of nitrification was detected, which was confirmed by a decrease in the concentration of ammonia nitrogen within the range 83 to 92%. The average efficiency of removing total nitrogen from the sewage was 67%. The efficiency of removing phosphorus compounds from the sewage was at the level of 82%. The results of the research on sewage treatment in the one-level wetland bed with the vertical flow of sewage VF-CW are comparable with those found in literature.

3.2. Polycyclic aromatic hydrocarbons

In the biofilter taken from hydrophytes wastewater treatment plant, total concentration of 16 PAHs varied between 32 and 42 µg/kg dm. According to the classification of the Institute of Soil Science and Plant Cultivation, the soils contaminated with PAHs at the total concentration not higher than 200 µg/kg dm. can be recognized as not polluted [31]. It should be emphasized that permissible concentration of nine PAHs ((naphthalene, phenanthrene,anthracene, fluoranthene, chrysene, benzo(a)anthracene, benzo(a)fluoranthene,



1- Naphthalene, **2** – Acenaphthene, **3** – Fluorene, **4** – Phenanthrene, **5** – Anthracene, **6** – Fluoranthene, **7** – Pyrene, **8 -** Benzo(a)anthracene, **9** – Chrysene, **10** - Benzo(j)fluoranthene, **11** - Benzo(b)fluoranthene, **12** - Benzo(k)fluoranthene, **13** - Benzo(a)pyrene, **14** - Dibenzo(a,h)anthracene, **15 -** Benzo(g,h,i)perylene, **16 -** Indeno(1,2,3,c,d)pyrene

Fig. 5. Chromatogram of plants samples (the example).

Table 1
The characteristics of raw wastewater and purified wastewater, mg/L

	1		2		3		4		5	
Series	S	O	S	O	S	O	S	O	S	O
BOD_5	212	13	192	23	275	11	311	42	188	23
COD	411	27	422	26	442	39	388	56	472	56
$N\text{-}NH_4^+$	63.0	7.6	79.0	11.6	71.0	6.3	88.0	14.4	54.0	4.2
$N\text{-}NO_3^-$	1.1	14.3	0.8	13.2	1.7	21.9	0.8	13.4	1.6	19.4
N_{tot}	83	24	91	24	88	32	94	31	74	27.4
P_{tot}	6.3	1.1	11.3	2.9	8.4	1.8	14.6	2.7	19.6	1.2

Note: S–raw wastewater, O–purified wastewater.

benzo(a)pyrene, and benzo(ghi)perylene), according to Polish standards, concerning limit values of PAHs in soils from protected areas is also equal to 1,000 μg/kg dm [32]. Carcinogenic PAHs constituted 32% of the total concentration of the hydrocarbons analyzed. Concentration of bezno(a)pyrene varied between 0.9 and 1.1 μg/kg dm. Compared to Polish legislation standards it must be stated that the concentration of BaP in soil exceeded the permissible value (20 μg/kg dm) for the protected area [32]. The percentage share of the groups of hydrocarbons sorted according to the number of rings in their particles is presented in Table 2. The concentrations of 2-, 3-, 4-, 5-, and 6-ring of PAHs in Fig. 6 are presented.

The percentage share of the groups of hydrocarbons sorted according to the number of rings in their particles was different than in the case of biofilter and parts of plant. 55% of total PAHs present in the biofilter were 3- and 4-ring compounds. In roots, the most abundant compounds were low-weight ones (naphthalene and 3-rings of PAHs). The dominant PAH compounds in stems were 5-rings of hydrocarbons. 66–68% of total PAHs present in leaves were 3- and 4-ring compounds. The share of carcinogenic compounds was lower in the biofilter (32%) than in the leaves (86–87%).

Concentrations of naphthalene in biofilter samples and in some parts of the plant are presented in Fig. 7. Naphthalene was the compound which was observed in the highest concentration in the samples of roots. This compound has volatile properties and it is not usually present on the surface of soil. Therefore, determination of naphthalene in soil is often omitted in literary sources. In this research, the concentration of naphthalene was low and did not exceed 8 μg/kg dm and it was lower than the concentration limit for the protected area (100 μg/kg dm) [32].

In Fig. 8, the concentrations of 3-rings (acenaphthene, fluorene, phenanthrene, and anthracene) of hydrocarbons are presented. The total contents of these compounds were in the range of 11–21 μg/kg dm. The dominant PAH compound in the biofilter and in parts of the plant was phenanthrene. The highest concentration of these compounds was in leaves of plants.

In Fig. 9, the concentrations of 4-rings (fluoranthene, pyrene, benzo(a)anthracene, and chrysene) of PAHs are presented.

Table 2
Percentage share of the groups of hydrocarbons sorted according to the number of rings in their particles

	% share in individual samples				
PAHs	Biofilter	Roots	Stems	Leaves	Surface of leaves
Naphthalene	21	26	12	–	–
3-rings of PAHs	29	25	20	31	32
4-rings of PAHs	26	23	27	35	36
5-rings of PAHs	18	20	31	24	27
6-rings of PAHs	6	6	10	10	5
Carcinogenic PAHs*	32	54	73	86	87

*Carcinogenic PAHs : BaA, Ch, BbF, BkF, BjF, BaP, DahA, BghiP, and IP.

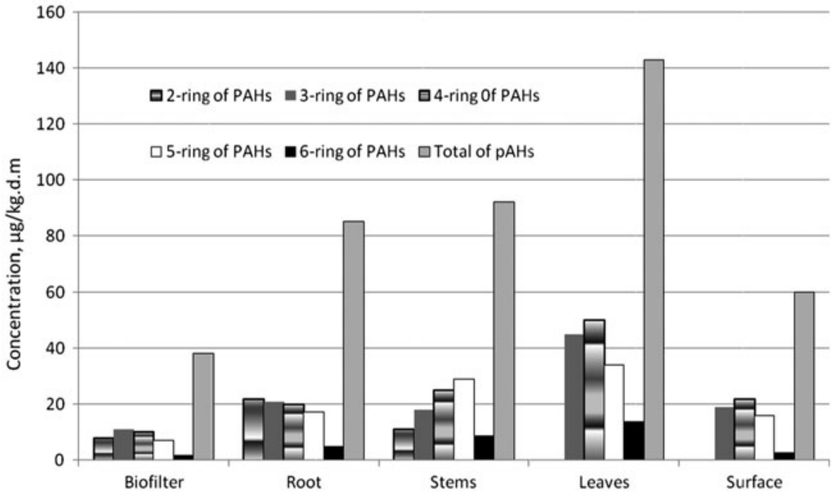


Fig. 6. Concentrations of PAHs in biofilter and in parts of plant.

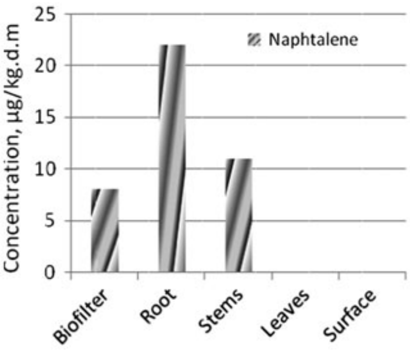


Fig. 7. Concentrations of naphthalene in biofilter samples and in plants.

The total concentration of 4-rings of hydrocarbons of these compounds varied between 10–50 µg/kg dm. The highest concentration of these compounds was in leaves of plants.

The concentrations of 5-rings (benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, and dibenzo(ah)anthracene) of PAHs are presented in Fig. 10. The lowest concentration of five hydrocarbons was in the biofilter and the highest concentration of these compounds was in the leaves. The average content of five hydrocarbons was in the range of 7,936 (biofilter)–34 µg/kg dm (leaves).

In Fig. 11, the concentration of 6-rings of PAHs in the biofilter and in the parts of plants is presented.

The concentrations of indeno(123 cd)pyrene and benzo(ghi)perylene were very low and did not exceed 7 µg/kg dm. The highest concentration of 6-rings of compounds was in extracts from leaves. 16 PAH compounds were present in roots, stems, and leaves of a plant taken from wetland. The highest concentration of PAHs total was obtained for leaves; it was on average equal to 143 µg/kg dm. The total concentration of PAHs in stems was on average equal to 92 µg/kg dm and was at the same level as in roots (85 µg/kg dm). However, comparing PAHs concentrations analyzed in various studies is difficult because majority of the results of research concerns the content of PAHs in soil, water, and air. A few articles refer to PAHs content in wastewater and in plants. There is no sufficient literature data referring to either the biofilter or plants taken from wetland treatment plants in technical conditions. A study on the plants is focused on the concentration of these compounds in plants for consumption, and while using plants to remediate the polluted soils.

Giraud et al. [33] investigated the process of degradation of selected PAHs during wastewater treatment. The studies were carried out on a pilot hydrophyte treatment plant and wastewater was contaminated with anthracene and fluoranthene, respectively. The results of the investigations proved the possibility of removing these compounds from wastewater by fungi. The level of the degradation of hydrocarbons did not exceed 70% [33]. Machate et al. [34] investigated the degradation of phenanthrene in five-stage hydrophytes of vertical–horizontal flow using the following species of plants: *Scirpus lacustris and Typha* spp. The level of removal of phenanthrene ranged up to 99.9% and it was similar both in the summer and in the winter. The highest decrease in the concentration of phenanthrene in wastewater was obtained after the first stage of treatment. A decrease in this compound

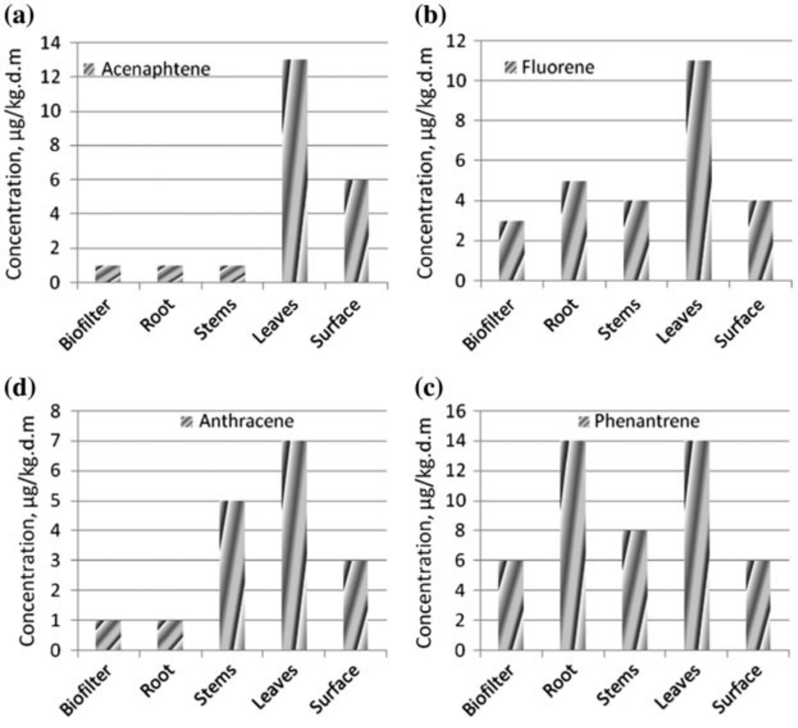


Fig. 8. Concentration of 3-rings of hydrocarbons: (a) acenaphthene, (b) fluorene, (c) phenanthrene, and (d) anthracene.

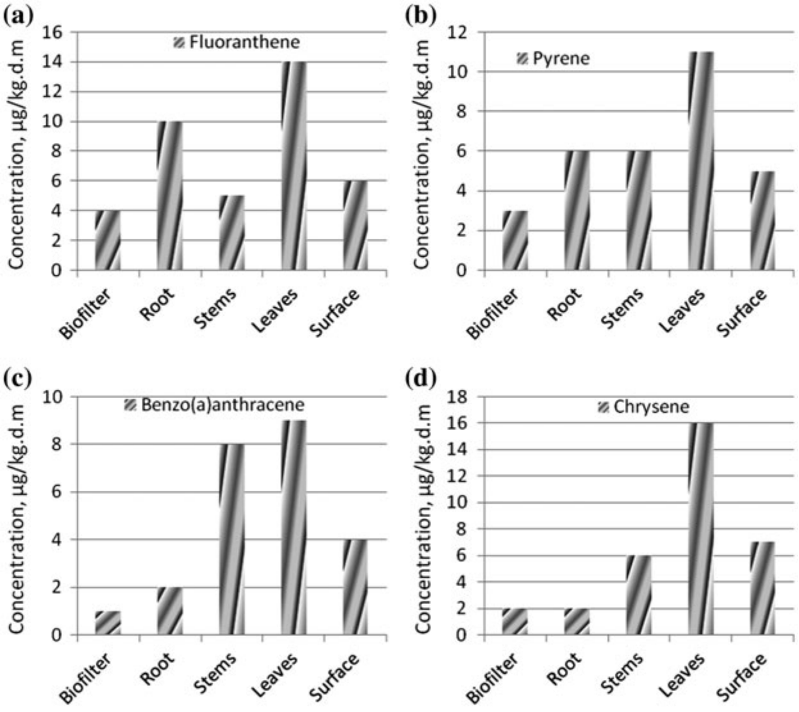


Fig. 9. Concentration of 4-rings of PAHs: (a) fluoranthene, (b) pyrene, (c) benzo(a)anthracene, and (d) chrysene.

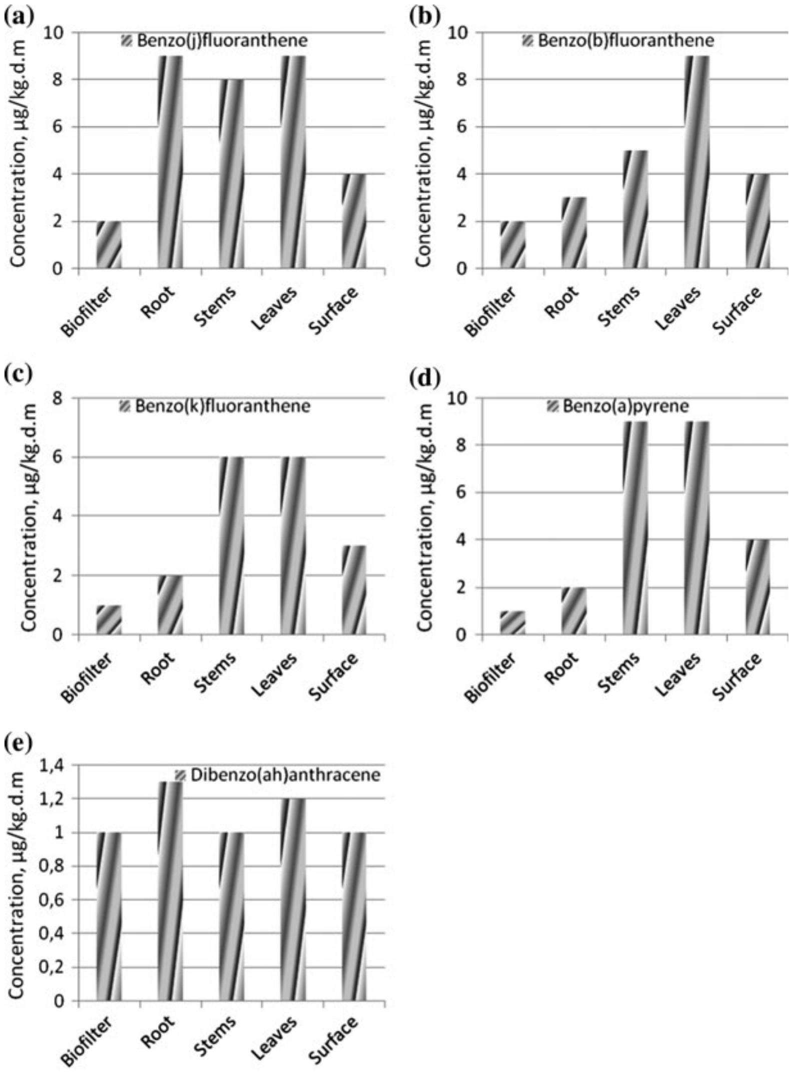


Fig. 10. Concentration of 5-rings of PAHs: (a) benzo(j)fluoranthene, (b) benzo(b)fluoranthene, (c) benzo(k)fluoranthene, (d) benzo(a)pyrene, and (e) dibenzo(ah)anthracene.

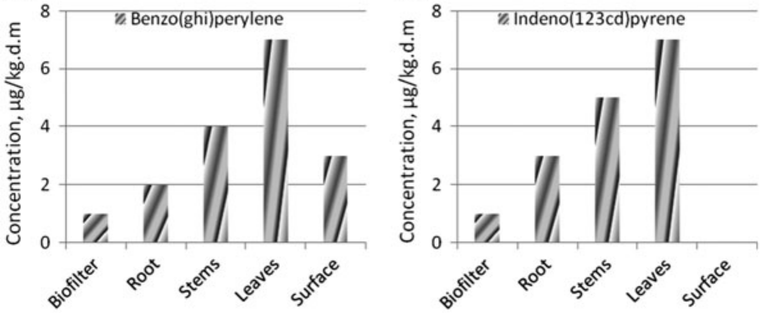


Fig. 11. Concentration of 6-rings of PAHs: (a) benzo(ghi)perylene, and (b) indeno(123 cd)pyrene.

depended on the time of wastewater in the treatment plant, hydraulic parameters such as: the flow rate and porosity of filling [34].

One of the co-authors carried out some investigation regarding the changes in the concentration of PAHs in wastewater during treatment. Wastewater was collected from a municipal sewage treatment plant, where the processes of mechanical, biological, and chemical phosphorus removal occurred. The concentration of PAHs in raw wastewater, after sedimentation processes, after the biological process and in the treated wastewater was determined, respectively. The average of 16 PAHs concentration reached 5.2 μg/L. in raw wastewater. During the process of sedimentation of mineral suspensions solids and after the process of sedimentation in primary settling tanks, the total concentration of PAHs was lowered by 40–47% compared to the initial contents. In the treated wastewater, the concentration of 16 PAHs was lowered by 78–93% from that of the raw wastewater and did not exceed 1.2 μg/L [35].

Some literature data confirmed that PAH contents in plants coming from contaminated soils gave the possibility of phytoaccumulation. It was found that the level of PAHs concentration in plants (dandelion, cabbage, parsley, carrot, and cucumber) depended on the amount of those compounds in soil [36,37]. The plants may metabolize hydrocarbons in the co-metabolic fates as well as they may cumulate reaction products in tissues e.g. roots. The fates are possible if hydrocarbons are available to the roots and they migrate through the stem [38–40].

Plants due to the fact that they are capable of PAH accumulation are used for phytoremediation of soils contaminated with these compounds. Rasmussen and Olsen investigated the effectiveness of removal of 3-rings of PAHs from soil using grass (*Dactylis glomerata*). It was found that the effectiveness of PAHs removal depended on the time contact with the polluted soil. It was proved that biodegradation in soil was stimulated by plants [41]. Plants such as: grass, leguminous plants, wild rye, oat, and wheat may be used to remediate the soil. For example, degradation of the pyrene and anthracene with the efficiency of 30–40% by leguminous plants was obtained. The efficiency of biodegradation was depended to the solubility of PAHs in water, quantity of micro-organisms population, and their enzymatic activity. It was proved that enzymes produced by roots of the plants intensify biodegradation of hydrocarbons [39]. Liste and Alexander [42,43] investigated degradation of pyrene using plants such as: oat, lupin, rape, fennel, parsley, pepper, and pine. After two months, the efficiency of removal of pyrene ranged 74% on soil covered by plants, whereas on control soil did not exceed 40%, respectively. This experiment proved that the removal effectiveness of this hydrocarbon did not depend on roots mass. Other investigations of those authors proved that plants could cumulate hydrocarbons by the transport from roots. In rhizosphere of plants cultivated on soil contained much more hydrocarbons (phenanthrene, pyrene) than the soils without plants [42,43]. Tao and co-authors [44] determined the dependence between the content of PAHs in cabbage and both in air and in soil. The level of pollution of studied samples by PAHs depended on the concentration of these compounds in the air, whereas dependence of the level of soil contamination was statistically insignificant [44].

In earlier studies of the co-author, the concentration of PAHs in soil amended with sewage sludge was analyzed. Furthermore, the concentration of 15 PAHs was also analyzed in particular parts of *Salix viminalis* taken from soil. Studies in plants from plantations are important taking into account their use in energy production. The average content of 15 PAHs in soil was 700 μg/kg dm. PAHs concentration in leaves (112–118 μg/kg dm) was on average twice as high as in stems (49–59 μg/kg dm) and roots (65–69 μg/kg dm) [45].

4. Conclusions

PAHs occur both in the natural environment and in plants. They may also be a biosynthesis product both of algae and of plants. However, comparing natural and anthropogenic sources of these compounds is difficult [46]. PAHs in plants are either metabolized or can be oxidized. Reaction products of these fates are accumulated in plants, especially in roots [38,39]. The transformation intensity of PAHs depends on the solubility of these compounds in water. Hydrocarbons are well soluble in water and can migrate in the plant, whereas insoluble compounds are adsorbed on the surface of the roots. The compounds adsorbed on the surface of the roots are not readily available for plants and for micro-organisms [44]. Other studies indicate that the roots stimulate the growth of micro-organisms which supports biodegradation of PAHs [39]. Comparison of the results of research conducted in the laboratory conditions with the results of studies in technical terms is difficult. This is due to the fact that most tests are conducted under laboratory conditions which are not present in the environment. Water or soils are spiked with a precise amount of PAHs and changes of their concentrations are monitored under laboratory conditions. Research in technical conditions is difficult due to changing environmental conditions and the presence of other factors that may have influenced the transformation of PAHs. In the content of PAHs, both biotic and abiotic transformations played an important role. An increase in the concentration of PAH both in plants and in the biofilter is significant for air deposition (rain or dry deposition). Also, both in plants and in the biofilter, natural biosynthesis, volatilization, and leaching of PAHs played an important role [47].

Based on the results of the experiments it can be concluded that:

(1) after 4 years of exploitation of a wetland treatment plant, the presence of PAHs in the biofilter and in plants was confirmed;
(2) the total PAHs concentration in the biofilter was at the level of 37 μg/kg dm; carcinogenic compounds shared 32% of the total concentration;
(3) the possibility of migration of hydrocarbons from roots to other parts of plants (stems, leaves) was confirmed;
(4) PAHs concentration in extracts from leaves (143 μg/kg dm) was higher than in stems (92 μg/kg dm) and in roots (87 μg/kg dm);
(5) PAHs present in extracts from the surface of leaves (60 μg/kg dm), demonstrates the ability of deposition of these compounds from the air.

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